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FINAL REPORT
A STUDY OF THE STATE-OF-THE-ART OF HERMETIC SEALS FOR SECONDARY ALKALINE SPACECRAFT CELLS

(1967 June 20 - 1968 March 20)

Contract No. NAS 5-10432

Prepared by

TRW Systems Group
One Space Park, Redondo Beach, California

for

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Goddard Space Flight Center

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ABSTRACT

A study was conducted of the current state-of-the-art of hermetic seals for secondary alkaline spacecraft battery cells, including seals now in use, those under development, and those potentially useful. Manufacturing, text, analysis, and performance data from the space field were collected and analyzed with the objectives of determining the degree to which existing seals satisfy current and future requirements, of identifying any deficiencies, and of providing guidelines for future seal research and development work that may be indicated. All known types of hermetic seals were reviewed for their applicability to alkaline cells and for a background for the study. Cell vendors, users, and test organizations were surveyed by questionnaire and most of them were subsequently interviewed.

Background information is presented in which the requirements for hermetic seals for spacecraft cells are developed, and a variety of hermetic seals used in other applications are reviewed for potential applicability to alkaline cells. Methods in use today for hermetically sealing spacecraft cells are then presented in detail, as well as those known to be under development for this application. Factors of design and manufacturing that are important for production of satisfactory seals are analyzed and compared to current practice. Failure modes, test methods, and test results are described and discussed.

It is concluded that, of the various methods available, ceramic-to-metal seals have the greatest potential for high reliability and long life. To achieve the potential, greater attention must be paid to the details of design, manufacturing, and quality control. Failure modes have been identified, but failure rates need to be established and failure mechanisms must be better understood. Performance requirements for seals need better definition so that uniform test standards and methods may be established, and accelerated test methods will be necessary to allow testing to keep pace with changing demands.

It is further concluded that glass-to-metal seals are not suitable for alkaline spacecraft cells unless they can be fully protected from the internal environment of the cell. Rubber-type seals are marginal, but more sophisticated designs appear capable of supporting at least 1-year missions. One specialized compression seal is particularly promising, having been tested for 5 years

without leaking. A clear indication of life expectancy of the most recent seal designs is not yet apparent from the test data available. Commercially available ceramic-to-metal seals have demonstrated a 2- to 4-year life before leaking, depending on the manufacturer.

Recommendations include the taking of more quantitative data on leakage during life tests; the use of only best-quality, ceramic-to-metal seals for longer flights; a program to upgrade the quality of existing seals; development of nondestructive and of accelerated test methods for evaluation of seals; investigation of the mechanism of alkaline attack and of the physics of failure of seals; and the preparation and use of a universal performance and test specification for hermetic seals on spacecraft cells.

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1. INTRODUCTION

This Final Report is submitted in partial fulfillment of NASA Contract No. NAS 5-10432: A Study of the State-of-the-Art of Hermetic Seals for Secondary Alkaline Spacecraft Cells. The general purposes of the work were to survey all known methods now in use or under development for achieving the required gastight, insulating closure; and to collect, study, and report manufacturing, test, and performance data from the space field that would provide guidelines for future research and development on seals.

The study was carried out in several phases: (1) a review of all types of hermetic seals potentially applicable to spacecraft cells; (2) a survey by questionnaire of manufacturers and users of sealed spacecraft cells; (3) personal visits and discussions with those manufacturers and users willing and in a position to make a significant contribution to the program; and (4) study and evaluation of information gained. A tabulation of response to the questionnaire sent to users and test organizations is presented in Appendix I. This information is amplified in the text. The responses received from the vendor questionnaire did not lend themselves to tabulation, and therefore the information is presented only in the text.

The authors wish to acknowledge the contribution of a number of organizations and individuals who contributed significantly to this study. The list of contributors is presented in Appendix II.

All three types of alkaline cells currently used in space, i. e., nickel-cadmium, silver-cadmium, and silver-zinc, were included in the study. However, emphasis was placed on nickel-cadmium technology, as a great many more nickel-cadmium cells have been used in space to date than silver electrode cells, primarily because of the higher reliability and greater cycle life capabilities of the nickel-cadmium system in secondary service. Furthermore, this report emphasizes ceramic-to-metal seals as they have been used on most nickel-cadmium cells flown and on all spacecraft-type cells commercially available today.

This report begins with a background discussion in which the requirements for hermetic seals for spacecraft cells are developed, and a variety of hermetic seals used in other applications are reviewed for potential applicability to alkaline cells. Methods in use today for hermetically sealing spacecraft cells are then presented in detail, as well as those known to be under development for this application. Factors of design and manufacturing that are important for production of satisfactory seals are analyzed and compared to current practice. Failure modes, test methods, and test results are then described, and the report concludes with a discussion of the foregoing information, with conclusions and recommendations based on the study.

2. BACKGROUND

2.1 GENERAL

The hermetic seals first used in spacecraft battery cells in this country were taken directly from the state-of-the-art at that time and as such were designed for entirely different applications. Those used on sealed nickel-cadmium cells, for example, where a metal cell case is involved, were essentially those developed by the vacuum-tube and related industries, i. e., glass-to-metal and silver brazed ceramic-to-metal types. It is now apparent that early alkaline spacecraft cells were fabricated and flown with testing inadequate to demonstrate compatibility of these seals with the cell internal environment. As is known, the early hermetically sealed alkaline cells were subject to a high percentage of seal failures in the form of leaks and shorted insulators. Fortunately, many of these occurred early in cell life, and the faulty cells were discovered during ground testing. The surviving cells were then flown with the hope that their seals would be inherently more resistant. The batteries were able to support the missions in most cases; however, mission life requirements were relatively short at that time.

As mission life was extended, battery faults began to occur in orbit with cells from certain manufacturers, primarily in the form of internally shorted cells. Although such shorting can occur by contact of positive with negative plates, it was assumed that shorting across the insulator seal was more probable, based on laboratory tests showing that unprotected silver in the ceramic-to-metal braze can migrate in the internal cell environment. Various fixes were developed, including at first covering the silver braze with an organic coating or with a plating of an inert metal, and later substituting other alloys for silver braze, retaining the protective coatings. These improvements, in conjunction with certain changes in mechanical design to reduce stresses, have resulted in a marked reduction in the incidence of early leakage and shorting, and presumably have resulted in seals with longer ultimate useful life than previously possible. Spacecraft life requirements are also increasing rapidly, however, and designs for missions lasting up to 10 years are on the drawing boards. Therefore, this study undertook to estimate the performance capability of state-of-the-art seals and those under development, and to compare the results with the requirements for present and/or projected missions.

2.2 DEFINITION OF REQUIREMENTS

The ultimate measure of an adequate seal is its ability to allow the battery of which it is a part to perform its mission. Electrical, reliability, and life requirements for the battery as a whole are usually well defined for each application. These requirements are translated to the cell level, and cell requirements imply certain terminal seal requirements. The relationship between seal requirements and cell requirements has not been clearly defined in the past, and is discussed below.

In considering seal life requirements, it is necessary to distinguish between the concepts of a seal failure, a cell failure, and a battery failure. As will be made clear in later discussion of failure modes, a seal can "fail" (in the sense that it no longer satisfies all specified requirements) on a cell without causing the cell to fail. For example, a seal may show obvious alkaline leakage for an extended period and yet the cell can show normal electrical performance. Or one of the insulators of a steel-encased cell having two insulated terminals can become shorted, yet if the other insulator is clean the cell can continue to operate normally. Also, one cell of a series-cell battery can "fail" by shorting, yet the battery need not necessarily fail, as an extra cell can be included in the design to assure that battery voltage is sufficient in case of a shorted cell, and/or electronic circuitry can be provided to compensate for a low-voltage cell. Boost regulators are also used to accommodate a wider range of battery voltage. A complete open-circuit cell, on the other hand, is much harder to compensate for, and usually results in a failed battery.

2.2.1 Cell Requirements

Calculation of the requirement for individual cell reliability from a given battery reliability is straightforward only if the failure of any one cell is assumed to fail the battery. This will be the case if the battery configuration consists of a single string of cells in series, with the minimum number of cells required to support the load, and with no protective circuitry used. This configuration places the greatest demand on cell and thus on seal reliability, and is used here as the basis of a calculation of cell reliability requirements. Thus for the simple series-cell battery:

$$R_{cell} = 1 - f_{cell}$$
$$\cong 1 - (1/N)f_{batt}$$
$$= 1 - (1/N)(1 - R_{batt})$$

where R is the reliability, f is the normallized failure frequency, and N is the number of cells in series. A range of battery reliability requirements typical of current spacecraft is shown in Table 1 with corresponding cell values for 10- and 20-cell batteries.

Table 1. Cell Reliability Requirements When One Cell Failure = Battery Failure

Battery Reliability Requirement:	0.98		0.99		0.995	
Number of Cells:	10	20	10	20	10	20
Cell Reliability Requirement:	0.998	0.999	0.999	0.9995	0.9995	0.99975

It can be seen that the range of permissible failure frequencies for cells is from 2/1000 to 2/10,000. These figures are the requirements at end of mission life. The permissible time-dependent failure rates are the above figures divided by the life requirement. Thus, for a battery reliability of 0.99, cell failure rate requirements for 20-cell batteries range from 1/2,000/yr for a 1-yr mission to 1/10,000/yr for a 5-yr mission.

2.2.2 Hermetic Seal Requirements

In the simple, series battery considered here, the battery will be failed if one or more cells become internally shorted or develop an open circuit. As either of these effects can be caused by terminal seal failures in a nickel-cadmium cell, the reliability and failure rate requirement of the seal is the same as that for the cell, when the cell has a single insulated terminal. When two insulated terminals are used, the failure rate for leakage must be half that for a cell, while that for shorting may be much greater because both insulators on the same cell must become shortened to short out the cell.

A review of commercial practice revealed no definition of a hermetic seal useful for battery cells. Requirements relative to the seals for alkaline spacecraft cells fall into the categories of leakage, insulation resistance, and other mechanical properties. These are discussed below.

2.2.2.1 Leak Rates

If the gas leak rate is assumed constant throughout the life of the cell, the maximum permissible leak rate is not a fixed number, but is proportional to the capacity of the cell and inversely proportional to the life requirement. For a nickel-cadmium cell, the maximum gas leak rate should be calculated from its effect on the excess negative plate charge capacity, rather than from its effect on the water content. Current practice is to fabricate sealed nickel-cadmium cells with the cadmium (negative) plates having about 20% excess capacity when the cell is in the charged state in order to avoid hydrogen evolution at the negative. When the cell remains sealed, this excess negative material, as $Cd(OH)_2$, is maintained during overcharge by recombination of oxygen generated at the positive plates. If, on the other hand, oxygen can escape through a leak, a side reaction takes place during overcharge which results in the conversion of $Cd(OH)_2$ to Cd as follows:

$$2\ Cd(OH)_2 \rightarrow 2\ Cd + O_2 + 2\ H_2O$$

As more and more O_2 is lost, this reaction may proceed until all the excess $Cd(OH)_2$ originally present is consumed.

The loss of excess negative capacity that may be tolerated is not a definite quantity since it depends on the method of operating the cell. A loss equivalent to 10% of the nominal cell capacity is considered by most to be the upper limit. Loss of 10% of cell capacity from the negative electrode corresponds to a maximum allowable leak rate of 0.7×10^{-6} atm cc O_2/sec/A-hr of cell capacity for 1-yr life, assuming that the leak rate is constant. The equivalent helium leak rate, calculated assuming that the leak rate is diffusion controlled, is 2.8 times that for 0_2, or 2×10^{-6} atm cc/sec/A-hr capacity for 1-yr life. Longer life requires a proportionately lower leak rate.

Sealed nickel-cadmium cells contain about 3 cc of electrolyte or about 3 g of water per ampere-hour of capacity. The loss of water from the electrolyte that may occur without impairing the cell is not known, but if it is assumed that water loss is to be limited to 10% over the mission life, then the maximum permissible leak rate is clearly 0.3 g/yr/A-hr capacity for a 1-yr life. Similar reasoning leads to a maximum loss rate of 0.1 g/yr of KOH per ampere-hour capacity for a 1-yr life requirement.

Other substances that may be lost from the cell interior through a leak are hydrogen gas, water (gaseous and/or liquid), and KOH. Hydrogen may be generated at the negative electrode during charging if excess negative capacity is not available, or at the positive electrode during overdischarge (reverse charging). If conditions are such that hydrogen is produced, and the cell leaks, then it is clear that both hydrogen and oxygen gas will be lost, as oxygen is generated during normal cycling. Loss of both H_2 and 0_2 results ultimately in loss of water from the electrolyte.

Loss of water in the form of a gas through a leak should be negligible, due to the relatively low vapor pressure of water in the cell. Water may also be lost as part of the material lost by "electrolyte leakage." This process results in an alkaline deposit on the outside surface of the cell; however, it is not necessarily synonomous with a gas leak, as discussed in Section 4.

2.2.2.2 Insulation Resistance

Insulation resistance is not so much a characteristic of the seal as it is of the terminal assembly as a whole. However, this property is so closely associated with seal technology in alkaline cells that it is included as part of the definition of a hermetic seal.

The requirement for insulation resistance is a function of the coulombic charge efficiency and self-discharge rate of the cell. For silver-cadmium and silver-zinc cells, which have charge efficiencies close to 100% and very low self-discharge rates, insulation resistance must be of the order of 10^5 ohms in order not to accelerate self discharge on open circuit.

This is usually no problem because of the plastic cases used. For nickel-cadmium cells, which have lower charge efficiencies, and for which the self-discharge rate is equivalent to several percent of cell capacity per day near full charge, insulation resistance need not be more than about 10 K ohms in order to have a relatively negligible effect on charge retention and charging efficiency.

2.2.2.3 Other Seal Requirements

Other general requirements of a satisfactory terminal seal assembly for alkaline spacecraft cells that do not directly affect hermeticity include sufficient mechanical strength to sustain applied stresses, sufficient electrical conductivity of the terminal post, ease of making cell-to-cell connections, ease of control and inspection during and after fabrication, and the inherent capability of retaining physical integrity throughout the design life of the application. Final evaluation of seal performance must consider all these factors.

2.2.3 Definition of Seal Failure

It was established above that a seal for these cells will not cause a cell to fail in 1 yr as long as the average helium leak rate is less than 2×10^{-6} atm cc/sec/A-hr capacity, water loss is less than 0.3 g/yr, and the resistance across the insulator remains greater than about 10 K ohms. Seal failure thus can be defined as failure to satisfy one or more of these requirements.

Although the above functional definition applies once the cell is in service, a different set of criteria, based on more stringent requirements, is needed for selection of cells for spacecraft batteries on the ground. This is because there is at present no way of knowing whether a leak or a partially shorted condition will become better or worse during flight, and therefore the assumption must be made that it will get worse. It appears desirable to be able to reject cells having seals with a leak rate or conductivity at least an order of magnitude less than that necessary to produce cell failure. Thus a helium leak rate of less than 2×10^{-7} cc/sec/A-hr capacity, a water leak of 0.03 g/yr/A-hr capacity, and a resistance (dry) of over 100 K ohms is required at the beginning of life.

The fact that cell selection criteria are not necessarily cell failure criteria tends to confuse failure histories and data. It is common practice to label a cell as "failed" when in fact it may only have failed to pass one of several arbitrary acceptance tests. More accurate terminology is needed in this area.

2.3 OVERALL REVIEW OF HERMETIC SEALING METHODS

This section presents the results of a general review of all known practical types of hermetic sealing methods and devices that could be used on alkaline spacecraft cells. The information obtained provided a necessary background for the study and was used as a basis for discussing the details of currently used seals with vendors and users of cells. Another purpose of this review was to reveal any types of seals that may be potentially useful for alkaline cell application but which are not now in use, and to determine the reasons.

Essential data on known hermetic seal methods are summarized in Tables 2 and 3.* Table 2 describes seals now commercially available, and Table 3 contains those not currently in use but on which some research and/or development has been done. Table 4 summarizes the properties of many of the materials used in insulator-to-metal seals. The following sections discuss the potential applicability of each of the different types of seals to alkaline battery cells.

2.3.1 Glass-to-Metal Seals

The main advantages of this type of seal are low cost, ease of manufacture, and the fact that the technology of glass-to-metal sealing is more highly developed than for any other type of hermetic seal. The obvious disadvantages for electrochemical cell application are the lack of sufficient strength in the glass to resist cracking in service and the reactivity of glass with the concentrated KOH solution used as the electrolyte in the cell. A less obvious problem with glass-to-metal seals arises from the nature of the glass-to-metal interface. Despite matching of bulk thermal expansion coefficients, the glass immediately adjacent to the metal remains under appreciable residual stress, and hence, the seal may be

*For source data see References 1, 2, 3, and 4.

perforated at the interface before the bulk glass phase has been appreciably attacked. The mechanism of this type of attack is discussed further in paragraph 4.1.1.

The exposed glass surfaces may be coated with KOH-insoluble materials to limit contact with the electrolyte. Any such coating must not only have essentially no porosity, but it must not permit KOH to penetrate between the metal or glass surface and the edges of the coating. KOH solution is known to be extremely powerful in destroying bonds between different classes of materials. Because of these problems, it appears that glass-to-metal seals are inherently unsuited for use as hermetic seals in alkaline electrochemical cells.

Table 2 lists two subtypes of glass-to-metal seals containing ceramic materials as part of the insulator phase, and Table 3 lists a "devitrified" glass-to-metal type. Although these variations appear to have higher strength in the nonmetal part, the bonds to the metal surfaces are glass-to-metal bonds, and because of this they offer little more promise than do conventional glass seals for alkaline cell applications.

2.3.2 Ceramic-to-Metal Seals

Ceramic-to-metal seals theoretically can be made free of both major problems associated with glass seals, i.e., the insulator is stronger than glass (although still fragile), and the insulator material can be selected to be insoluble in KOH solution. Although the sintered metal powder process ("moly-manganese" process) and the active metal process for metallizing ceramics seem to be equally adaptable to alkaline cells, in practice it appears that a successful powdered metal process requires either the use of a ceramic having a relatively high percentage of glassy phase, or the use of a glass between the ceramic and the metallizing. Thus, ceramic-to-metal seals made by this process are more prone to leakage in alkaline cells than are those made by the active metal process.

The presence of a brazing alloy introduces a potential problem area not present in glass-to-metal seals. Although theoretically completely stable braze materials might be selected for any application, the bulk of experience has been with silver alloys, primarily because the physical characteristics of the resulting product for conventional applications have been found to be far superior to those of seals made without silver in the braze. It is now known that silver is not stable in the braze when used with nickel-cadmium cells, but this was not anticipated from the known properties of silver alloys at the time these seals were first used in alkaline cells. A number of nonsilver-containing braze alloys are being used successfully in other applications, and presumably could be used in cells.

Brazing alloys are eliminated altogether for very high temperature applications, as indicated in item 2 of Table 3. Although this approach theoretically gives a completely stable joint, the primitive state-of-the-art and the high cost make them unattractive for spacecraft cells at this time.

Another variation of a ceramic-to-metal seal not requiring a brazing alloy is the graded cermet type (see item 3, Table 3). Investigated for use in high temperature vacuum and vaporized metal enclosures, this basic approach should be entirely satisfactory in alkaline cells from chemical and electrochemical standpoints. This seal is yet to be used commercially because of unsolved difficulties in the manufacturing process.

2.3.3 Compression Seals

Compression seals depend primarily on pressure between a metal surface and a compressible material surface. Compression seals made to be hermetic usually have metal bonded to nonmetal surfaces, and thus do not depend on pressure alone. The three types of compression seals in use are described in Tables 2 and 3. The elastomer seal is usually made in a flat, layer-like configuration. The polymeric (nonelastomeric) seals are made in the flat configuration and as a packing gland (e. g., with the polymer as a "chevron" packing), while the powder seal is made only as a packing gland. Two advantages of this approach for battery cells are that the compliant material can be chosen to be chemically inert in the cell internal environment, and the compliance is sufficient to prevent stresses on the seal due to the weight and relative motion of the electrode structure.

One special configuration of a compression seal is known which appears to take maximum advantage of the potential of this sealing principle. It is referred to as the Ziegler seal, named after the inventor, and is the subject of U. S. Patent No. 3, 109, 055. A unique feature of this design is that compression is radial to, rather than parallel to, the long axis of the conductor.

This type of seal is not subject to the chemical problems associated with glass-to-metal and ceramic-to-metal seals, but could be troubled with cold flow and possibly by deterioration from exposure to radiation. Further details are presented in paragraph 3. 1. 6.

The ability of the compressed powder seal (see item 4, Table 2) to hold KOH is not known; the fact that the powder is unconsolidated suggests that KOH solution may penetrate, especially if the original compression is relieved over a period of time by compaction of the powder. This, coupled with the mechanical complexity and weight of these devices, makes them relatively unattractive for spacecraft use.

2. 3. 4 Rigid Plastic-to-Metal Seals

Hermetic seals in which rigid plastics are bonded directly to metal conductors are rarely used outside the battery industry because of their severe limitations of mechanical strength, temperature range, and pressure range. They do play a useful role with plastic cell cases, however, and the technology for this application is discussed in subsection 3. 2.

Table 2. Summary of Hermetic Seals Commercially Available

Type of Seal	Subtype	Characteristics	Typical Materials	Fabrication Process	Inherent Advantages	Inherent Limitations	Producibility	Applications Experience
(1) Glass-to-metal	(a) Matched seals.	Expansion coefficients of materials are matched to minimize stresses.	Kovar, Mo, or W with hard glass (borosilicates). Fe or N: alloys with soft glass (lead).	Metal parts chemically cleaned and oxidized. Glass applied in plastic state under slight pressure. Metal parts etched and plated.	Seal design flexibility due to matched expansion. Characteristics. Inspectable seals.	Low resistance to attack by alkali solutions. Low radiation resistance.	Mass produced on a commercial basis.	Electronic devices (diodes and transistors); electrical feed throughs. Some alkaline cells.
	(b) Unmatched seals.	Thermal expansion coefficients not matched, metal ring designed to hold glass in compression.	Fe, low carbon steel, or stainless steel with soft or hard glass.	Similar to process for matched seals but oxidation of metal not required.	Wider selection of metals than for matched seals. Lower cost.	Hermeticity restricted to a lower temperature than matched seals. Low radiation resistance.	Same as 1 (a).	Same as 1 (a).
	(c) Mixed ceramic and glass.	Combines a mixture of glass and ceramic to obtain a low temperature seal.	Same metals and glasses as in 1 (a) and 1 (b) plus variety of ceramics.	Ceramic has high glass content which bonds to metal when brought to temperature. Forms glass-to-metal type seal.	Permits fabrication of complex assemblies with wide selection of materials. Relatively low temperature sealing process for ceramic parts.	Expansion characteristics not matched, limit on temperature range and chemical resistance.	Good.	Not widely used, in view of 2 (b).
	(d) Glass-coated ceramic.	Ceramic insulator is coated with glass or glass-metal frit to obtain low temperature seal.	Same as 1 (a) plus glass frit. Also a variety of metal-glass frits.	Intermediate layer of glass frit or glaze between ceramic and metal forms glass-to-metal seal. Fabrication in H_2 eliminates chemical cleaning.	Same as 2 (a), dimensional control.	Same as 2 (a).	Good	Widely used for low temperature metallizing and solder-sealed assemblies.

Table 2. Summary of Hermetic Seals Commercially Available (Continued)

Type of Seal	Subtype	Characteristics	Typical Materials	Fabrication Process	Inherent Advantages	Inherent Limitations	Producibility	Applications Experience
(2) Ceramic-to-metal	(a) Sintered metal process.	Strong, high temperature seals useful with a variety of alloys and ceramics.	Kovar, Mo, Cu, Ni, monel, or stainless steel; high-alumina ceramics; Mo- or W-based metallizing powders; various brazing alloys.	Ceramic is metallized by firing with refractory metal materials in controlled atmosphere. Metallizing is electroplated and metal parts are brazed to metallic areas.	No critically sensitive variables to process, withstand high temperatures and thermal shock, excellent dielectric properties, hermeticity, radiation resistant, nonmagnetic metal powders.	Ceramic-to-metal bond relatively easily attacked by KOH	Produced on a commercial scale. Most widely used seal in industry today.	Same as 1 (a) although not as widely used. Used extensively for power electron tube enclosures. Used on some spacecraft cells.
	(b) Active metal process.	Same as 2 (a) with less selection of materials.	Kovar or Mo metal parts, high-alumina ceramics, metallizing with Ti or Zr hydrides or metal powders, Ag or Ni transition brazing metals.	Process requires that all parts and materials be assembled in position during a one shot vac. firing operation. At high temperature, materials in contact react to form a strong chemical bond.	Same as 2 (a) except more critically sensitive to processing variables.	Seal fabrication processes are critical (assembly and purity of materials), silver migration from brazing alloy possible.	Relatively difficult.	Used on power electron tube enclosures and alkaline cells.

Table 2. Summary of Hermetic Seals Commercially Available (Continued)

Type of Seal	Subtype	Characteristics	Typical Materials	Fabrication Process	Inherent Advantages	Inherent Limitations	Producibility	Applications Experience
(3) Compression	(a) Elastomer-to-metal seal	Rubber-like insulating materials are bonded to metal parts and are under compression.	Many metals. Elastomers, selected on basis of properties required: neoprene, butyl rubber, Hypalon.	Combination chemical process (Vulcanizing) and heat and pressure used to bond elastomer to metal.	Same as (4). No critical processing steps required.	Same as (4) except reproducibility is relatively good. Loss of elasticity.	Not determined.	Used for a variety of applications. Have been tested on spacecraft cells.
	(b) Synthetic polymeric material-to-metal seal	Insulating material is compliant but not elastic.	Various metals. Polymeric materials such as Teflon, Kel-F, Nylon.	Adhesive bonding of polymeric material under compression. Seal design maintains polymeric material under compression.	Polymeric materials can be selected for specific properties required such as chemical resistance, strength, etc.	Large seal area required; temperature limited; poor bonding characteristics; high degree of compression required to maintain seal; cold flow problems.	Readily producible although may be complex design.	Used in alkaline cells where life and hermeticity requirements are not severe.
	(c) Powder seal	Ceramic-like powder is used as gasket under compression.	Any metals and inert powders.	Gland is machined with threaded cap. Powder is cast as cylinder around conductor. Cap is tightened to crush powder and make seal.	No critical steps. Holds high pressure at high temperature. Can be repaired by user.	Relatively large and heavy. May contaminate container. Hermeticity not known.	Good.	Used widely for high-pressure feed-throughs ("Conax").
(4) Rigid plastic-to-metal		Metal terminals are bonded to plastic with adhesives.	Acrylonitrile/styrene copolymer plastic, (Union Carbide bakelite C-11 molding cpd.), Epoxy adhesives, plated metal terminals.	Seal is made by casting sealant around metal terminal.	Uses commercially available materials; low cost; no close tolerances required; one step operation.	Mechanically weak; fragile bond; temperature limited; pressure limited; poor reproducibility.	Produced on a commercial basis.	Used on alkaline cells.

Table 3. Summary of Hermetic Seals Not Commercially Available

Type of Seal	Subtype	Fabrication Process	Inherent Avantages	Inherent Limitations	Applications Experience
(1) Glass-to-metal	Devitrified	Joints are made by conventional glass-to-metal manifacturing methods; then the glass is converted to a ceramic by heat treatment.	Conventional glass-to-metal manufacturing processes utilized. Chemical properties could be varied.	Process control problems unknown.	No known commercial use of process in this country.
(2) Ceramic-to-metal	(a) Direct fusion of ceramic-to-metal	Ceramic and metal parts are fused together directly under high-intensity beam of electrons.	Variety of metals and ceramics can be joined by this process.	Undeveloped state-of-the-art.	Tab welding to micromodule substrates has been shown to be feasible.
	(b) Oxide brazing	The ceramic is fused to metal member by melting suitable oxide eutectic between mating parts.	For use in joint which must withstand temperature above 1200°C.	Impractical on large pieces.	Research and development stage.
(3) Graded cermet		Successive layers of metal powder gradually enriched with ceramic powder are bonded together with heat and pressure to provide a seal between essentially metal and ceramic parts.	No abrupt interfaces on macroscale; no braze material to corrode.	Complex fabrication process; feasibility not not yet demonstrated; strength may be low.	No commercial application to date. Special high temperature for corrosive environment produced at Westinghouse.
(4) Compression	Synthetic polymeric material-to-metal (Ziegler seal)	Metal tube is compressed about polymeric material through which extends a metal conductor.	Ease of assembly; no braze problem; materials relatively stable chemically.	Producibility, reproducibility, and adaptability to large sizes unknown at present.	Laboratory testing only using Ni-Cd cells.

Table 4. Properties of Materials Commonly Used in Glass-to-Metal and Ceramic-to-Metal Seals

Material	Coefficient of Thermal Expansion (μin./in./°C) (25° to 300°C)	Melting* Point (°C)	Chemical** Resistance	Remarks
Metals				
Molybdenum	5.5	2625	Poor	Hard glass seals
Nickel-iron alloys (Alloy 42 and Kovar)	4.5 to 5.2	1450	Fair	Low electrical and thermal conductivity, hard glass and ceramic seals
Tantalum	6.7	2995	Poor	Hard glass seals
Stainless steel (Ni-Cr-Fe)	18.2	1400	Good	Ceramic seals
Nickel	14.6	1450	Excellent	Ceramic seals
Cold rolled steel (SAE 1010)	13.5	1450	Poor	Soft glass seals
Monel (Ni-Cu)	15.0	1350	Excellent	Ceramic seals
Copper	16.4	1083	Fair	All seals
Chrome iron	9.0	1400	Fair	Soft glass seals
Braze alloys				
Silver		960	Poor	100% Ag
Copper-silver eutectic		779	Fair	28% Cu; 72% Ag
Copper-silver		750	Fair	28% Cu; 65% Ag; 5% Mn; 2% Ni
Nickel-gold (NIORO)		950	Excellent	18% Ni; 82% Au

*The temperatures given in the melting point column are 1) the melting point temperature for metals, 2) the safe operating temperature for the ceramics, and 3) the softening point temperature for glasses.

**In the internal cell environment.

Table 4. Properties of Materials Commonly Used in Glass-to-Metal and Ceramic-to-Metal Seals (Continued)

Material	Coefficient of Thermal Expansion (μin./in./°C) (25° to 300°C)	Melting Point* (°C)	Chemical Resistance	Remarks
Ceramics				
Alumina (Al_2O_3)	6.5	1700	Excellent	Not attacked by alkali solutions
Steatite ($MgO \cdot SiO_2$)	6.9	1000	Good	Not attacked by alkali solutions
Forsterite ($2MgO \cdot SiO_2$)	10.0	1000	Good	Not attacked by alkali solutions
Zircon ($ZrO_2 \cdot SiO_2$)	4.4	1100	Good	Not attacked by alkali solutions
Glasses				
Soft glasses (Soda-lime and lead glasses)	9.0	620	Poor	Slowly soluble in alkali solutions
Hard glasses (Borosilicates)	4.6	700	Fair	More resistant to alkali than soft glasses

*The temperatures given in the melting point column are 1) the melting point temperature for metals, 2) the safe operating temperature for the ceramics, and 3) the softening point temperature for glasses.

3. CURRENT PRACTICE IN SEALS FOR ALKALINE SPACECRAFT CELLS

This chapter presents details of configuration, materials, and manufacturing processes for seal assemblies that are presently being used on spacecraft cells, and those which are in the process of being developed for this specific application.

Terminal seal assemblies currently available on spacecraft quality cells utilize ceramic-to-metal seals alone, ceramic-to-metal seals in combination with glass-to-metal seals, or rigid plastic-to-metal seals. No simple glass-to-metal seals are now used, although they have been tried in the past. Ceramic-to-metal seals are used on all sealed nickel-cadmium cells, as these are supplied only in metal cases. The rigid plastic-to-metal seals are supplied on sealed silver-cadmium and silver-zinc cells, the space-qualified variety of which are available only in plastic cases. Silver-cadmium and silver-zinc cells may be obtained in metal cases, but this design has not been proven to be reliable to date.

3.1 HERMETIC SEALS FOR NICKEL-CADMIUM CELLS

At the present time truly hermetically sealed spacecraft-quality nickel-cadmium cells are available as standard items from three vendors in the United States: Gulton Industries, General Electric, and Sonotone Corporation. Eagle-Picher offers nickel-cadmium cells on a custom-made basis utilizing one of several different terminal seal arrangements. Gould-National does not offer sealed cells at this time. Paragraph 3.1.1 covers only the more standardized designs available from Gulton, G.E. and Sonotone. Paragraph 3.1.2 discusses certain sealing methods commercially unavailable now, but which are under development or have been tested for use on nickel-cadmium cells.

3.1.1 Seals Now Commercially Available

3.1.1.1 The Gulton Ceramic-to-Metal Seal Assembly

One typical configuration of a terminal assembly using a ceramic-to-metal seal is shown in cross section in Figure 1. This type is currently used by Gulton Industries on all their standard spacecraft sealed nickel-cadmium cells, which are encased in stainless steel. The terminal post, ceramic insulator, and cell cover, common to all such assemblies, are designated by A, B, and C, respectively, in the figure. Cup I is a separate part used to facilitate the lower brazing operation. Part H is a relatively flexible metal collar used to reduce stress on the ceramic-to-metal joints and to provide matching of expansion coefficients at the upper ceramic-to-metal interface (D). A variation on this configuration, in which the insulator (B) is brazed directly to the cover (C), and in which the cup (I) is machined integral with the terminal post, is available from Gulton, and is standard with Eagle-Picher.

This assembly of Figure 1 employs four braze joints: two metal-to-metal (E and G) and two ceramic-to-metal (D and F). One surface of each braze faces the inside of the cell. Protective coatings are used on all internal braze surfaces. Eagle-Picher uses a protective coating on the outside surfaces of the brazes and ceramic whereas Gulton does not. Some of the details of protective coatings are subject to variation at the request of the user.

The exact composition of certain materials is considered proprietary by manufacturers. It was learned that the ceramics being used were at least 85% Al_2O_3 and were probably 95+% Al_2O_3. The nature of the remaining percentage was not disclosed.

The cell cover is normally Type 304 or 304L stainless steel; the terminal post is 304, Alloy 52 (nickel-iron), or nickel, as the customer may require; and the collar (H) and cup (I) are Alloy 42. Alloy 42 has a coefficient of thermal expansion close to that of Kovar, which, as shown in Table 4, matches that of alumina.

The braze alloy used by Gulton is a silver-copper eutectic containing 78% silver (see Table 4). All metal surfaces on the underside of the cover assembly are plated with nickel by Gulton. Eagle-Picher uses a coating of epoxy resin on and in the immediate vicinity of the braze areas only. No organic coatings are used by Gulton in connection with the seal assembly.

The ceramic-to-metal bonds of the seal assembly of Figure 1 as supplied by Gulton are formed using the active metal process. This process is based on the fact that titanium or zirconium metal adheres strongly to oxide surfaces in the absence of a fluxing phase. The titanium or zirconium atoms are attracted to the oxygen atoms of the ceramic with which they can share an electron to satisy their valance requirements. After the first layer is deposited, additional atoms become attached by conventional metallic bonds.

In the process used for manufacturing the Gulton seal, a metal hydride is applied to the ceramic in an organic carrier. The coated ceramic is placed in a holding fixture along with the mating metal components and preforms of braze alloy. The fixture is placed in a vacuum oven, pressure is reduced, and heat is applied. The hydride decomposes during heating to the brazing temperature (approximately $1700^{\circ}F$), and the surface is metallized and alloyed with braze in one step. Gulton carries out this operation in-house. Eagle-Picher procures these cover assemblies from an outside vendor.

3.1.1.2 The General Electric Ceramic-to-Metal Seal

A somewhat different configuration of ceramic-to-metal terminal seal assembly, supplied by the Battery Products Division of General Electric on their nickel-cadmium cells, is shown schematically in Figure 2. This assembly, like the Gulton design, is composed of two intermediate metal piece parts (H and I) and has four braze joints. The main difference is that the post-to-ceramic braze joints (D and E) are made at the top of the insulator instead of at the bottom. In the standard G.E. cell design, the void space between the cup I and the ceramic and between the post and the hole through the ceramic is filled with epoxy resin (J). The resin coating is extended to cover the underside of the ceramic cylinder and the inside surface of braze F, as shown in Figure 2. G.E. also recommends that the outside surfaces of brazes F and G be coated.

The materials used are essentially the same as those in the Gulton assembly with the exception of the braze material, which is a silver-copper alloy containing a small percentage of palladium, and the protective coating system, which is an epoxy resin.

The ceramic-to-metal joints are made by Ceramaseal Corporation using the active metal process; process details are claimed to be proprietary. The terminal seals are procured by G. E. as complete cover assemblies, except for the epoxy resin, which is applied at G. E.

3. 1. 1. 3 The Sonotone Triple-Seal

The hermetic seal currently offered by Sonotone on its spacecraft-type nickel-cadmium cells consists of a ceramic-to-metal seal enclosed by two glass-to-metal seals. This configuration, referred to as the triple-seal, is shown diagrammatically in Figure 3.

On small cells (less than 3 A-hr) the terminal post (A) is a small-diameter solid rod. For larger cells, the post is a tube, used so that the thin wall gives glass-to-metal and ceramic-to-metal joints with lower residual stresses. The assembly is built into a heavy-walled collar (H) that is welded onto the cover (C). The ceramic insulator (B) is used to make the true hermetic seals at D and E. Glass at F and G, bonded to metal members A and H with conventional glass-to-metal seals, completes the assembly.

The terminal post and collar are made of high-nickel-iron-alloy (exact composition not disclosed). The ceramic is a high-purity alumina and the braze material is a gold alloy. Sonotone claims that a special alkali resistant glass has been developed for use in this assembly. No protective coating is now used on the glass surface facing the inside of the cell, since no coating has been found by Sonotone that adheres permanently in the presence of the electrolyte.

The assembly described above is fabricated by first welding the collar to the cell cover, then forming the ceramic-to-metal seals, then adding the glass. The mating surfaces of the ceramic insulator are metallized using the moly-manganese process. Sonotone purchases the ceramic metallized, then carries out the remaining operations in-house. Further details are considered proprietary.

In Sonotone cells using this seal, the weight of the electrodes is not borne by the terminal assemblies. Instead, the electrode structure is held in a sling that is attached to the cover of the cell. Axial stress and shear forces in the seal are thereby kept to a minimum.

3.1.2 Seals Under Development

The following sealing concepts and devices are not currently available, but are in various stages of development or testing. They are discussed under nickel-cadmium cells because they are for use with metal cell cases.

3.1.2.1 Experimental Ceramic-to-Metal Seals

Gulton has experimented with an improvement to their seal assembly consisting of a cap brazed onto the top, closing off the crevice between the terminal post and the hole through the insulator. The ceramic-to-metal joint is made on the top of the ceramic cylinder, not on the sides. No significant test results are available as yet. This effort is currently inactive because of a lack of apparent interest on the part of users.

A redesigned ceramic-to-metal seal employing a new metallizing process and a nonsilver braze alloy is currently under development by General Electric. The configuration is shown in Figure 4. Note that most brazed surfaces are normal to, rather than parallel to, the direction of shear. This type of configuration has been referred to as a "shear seal." Little information is available on the manufacturing process to date. The metallizing process is claimed to be new, does not involve either the active metal hydride process or the moly-manganese process, and is capable of bonding metals to practically pure alumina. The braze alloy is described as essentially pure nickel, hence silver migration is eliminated. Qualification testing is currently in progress and samples should soon be available for testing.

Another shear seal approach, similar in principle to that described above, has been partially developed by the Tube Division of RCA. A photograph of a section of one of these terminals installed in the cover of a cylindrical cell is shown in Figure 5. The metallizing process was not disclosed, but the braze is a gold alloy containing no silver. Limited testing has been conducted by RCA and it is claimed that no leakage was observed.

3.1.2.2 Experimental Compression Seals

A number of different elastomeric seals, generally of the compressed flat washer design, have been fabricated and tested on nickel-cadmium cells over the past few years; but, because of continued high incidence of alkaline leakage, cells having such seals have not been flown, and improved designs are being tested.

The configuration illustrated in Figure 6 represents one of the latest advances in the art of this type of seal. The particular seal shown is known as the Plitt seal and is currently under test by NASA. The terminal, electrically inert member (elastomer), and cell cover are shown at A, B, and C, respectively. There are two elastomer-to-metal bonded interfaces in the assembly. One occurs at D between the cell cover and the elastomer, and the other is at E between the lower, expanded portion of the terminal and the elastomer. The hermetic seal is effected by a combination of compression and adhesion. The compressive force of the assembly is produced by nuts (F) which are threaded onto the upper portion of the terminal. To eliminate a metal-to-metal contact between the nuts and the cell cover, a flat metal washer (G) and a flat elastomer washer (H) are placed between the nuts and cell cover. Most of the stresses produced in this type of seal are relieved by deformation of the elastomer; thus, this type of seal does not have to be specially designed to relieve stresses. The adhesive action is produced either by a vulcanization process or through the use of an adhesive between the mating elastomer and metal surfaces.

Metals and elastomers can be selected on the basis of their inherent chemical resistance and other properties. Some elastomer materials which have been utilized are the synthetics such as neoprene, butyl rubber, and Hypalon. In the Plitt seal currently under test, the elastomer is a molded neoprene containing no plasticizer. The material used to effect the adhesive bond between the elastomer and metal is Acloprene L100 containing MOCA curing agent. The flat elastomer washer of the seal assembly is also made of neoprene. The cover of the case is stainless steel.

The Ziegler seal (introduced in paragraph 2.3.3) has been tested on nickel-cadmium cells by the Bell Telephone Laboratories but is not currently being considered by Bell because they have no requirement in-house. It is a compression seal using a nonelastic insulator. A cross section of the assembly is shown in Figure 7. The seal is composed of an internally threaded, relatively heavy walled, metallic sleeve (D) that surrounds an externally threaded, cylindrical dielectric bushing (B) provided with an axial bore through which the terminal conductor (A) extends. The conductor, bushing, and sleeve are under heavy radial compression to form the seal. Because the dielectric bushing has some degree of plasticity, it can partially absorb any thermally or mechanically induced stresses.

The metallic sleeve of this assembly can be formed from nickel or high-nickel steel alloys. The material used by Bell Laboratories for the bushing was a polytrifluorochloroethylene, purchased under the trademark "Kel-F." Other organic polymeric dielectrics having properties comparable to polytrifluorochloroethylene might also be used. The material of the terminal electrical conductor is dictated only by the needs of the internal operation of the cell, being under no constraint by the seal process.

The effectiveness of this seal assembly is dependent upon the proper mating of the internal threads of the metallic sleeve with the external threads of the dielectric bushing. In order to prevent alternate high and low pressure regions, the crest of the threads must be rounded. In addition, to make the internal and external threads conform to each other as closely as possible, the difference must be substantially the same between the major diameter of the external thread and the major diameter of the internal thread, between the minor diameter of the external thread and the minor diameter of the internal thread, and between the pitch diameter of the external thread and the pitch diameter of the internal thread. These requirements make the thread-cutting operation the most critical step during manufacturing.

During assembly of the cell, the metal sleeve (D) is first welded to the cell cover. The terminal post (A) is then extended through the metal sleeve as the cover is placed on the case. After the cover is secured to the case, the bushing (B) is slipped onto the post and threaded into the sleeve. The seal is effected by radially compressing the sleeve about the bushing. The compression is performed by a tool that applies a substantially uniform compressive force to the entire circumference of the portion of the metallic sleeve. Some experimental cells utilizing this type seal have been on a continuous overcharge at the C/10 rate and room ambient temperatures for 5 yr with no seal failures or apparent degradation .

3.2 HERMETIC SEALS FOR SILVER-CADMIUM AND SILVER-ZINC CELLS

Because silver-cadmium and silver-zinc cells have been used in sealed, secondary batteries for space missions much less frequently (and then for short missions only) than have nickel-cadmium cells, the state-of-the-art of hermetic seals for silver-type cells is less advanced. Only plastic cell cases are currently in use. The two seal problems encountered with plastic cell cases are: (1) sealing between the metallic electrical conductors and the plastic case material and (2) sealing between plastic parts, primarily sealing the cover to the main body of the cell case. Only the former seal problem is included in this study.

Silver-cadmium and/or silver-zinc cells of the "sealed" type are offered by several vendors, but they are not claimed to be hermetically sealed. The degree of hermeticity is left up to the user to determine according to his own requirements.

Several different approaches are in use for making the plastic-to-metal seal. These are designated as: (1) the standard vendor-supplied integral type, (2) the user-developed integral type, and (3) the potted type. The essential features of each of these are presented below.

3.2.1 Standard Vendor-Supplied Integral Seals

The terminal seal most readily available from cell vendors is one in which the terminal posts are cast and/or cemented into the cover. A typical example of a cemented type, having a threaded stud for making external connections, is shown in Figure 8. The terminal is usually brass, and may be silver plated. The cement is either an epoxy resin or a proprietary formulation known as PS-18.

3.2.2 User-Developed Integral Seals

Because of unsatisfactory experience with the type of seal described above, some users have, in cooperation with vendors, developed more sophisticated terminal seal assemblies, one of which is shown in Figure 9. In this configuration, an O-ring is used in addition to the plastic-to-metal joint to make the seal. The terminal post is internally threaded at the top and a screw is used to fasten external connectors in order to reduce weight relative to an externally threaded stud. This design is being implemented for the Apollo reentry and post-landing silver-zinc battery.

3.2.3 Potted Seals

It is generally agreed that sealing in addition to integral terminals is desirable for sufficient reliability over a longer time period. This is usually accomplished by potting the tops of the cells and/or potting the entire terminal surface of the battery after the cells have been assembled and the connections made. Potting the entire assembly provides the additional benefit of sealing any leaks at the cover-to-case junctions and of filling any void spaces between cells, thereby making the cases able to withstand higher internal pressure without cracking. A photograph of one such assembly, using silver-cadmium cells, is shown in Figure 10. This unit was developed by NASA Goddard for use on IMP A, B, and C.

Another approach, developed by JPL for use on silver-zinc batteries flown on Mariner and Surveyor missions, consists of sealing each plate lead individually as it leaves the cell. A compartment is provided at the top of the cell, through which the plate leads pass, to facilitate potting. The leads are given a convoluted shape to maximize the length that is embedded in the potting. In addition, the entire assembly is potted together to provide an overall seal barrier. An epoxy resin is used for potting; Shell Epon 815 with TETA as a curing agent has been found satisfactory. In approximately 70 batteries built for JPL using this method, no leakage has been detected. The weight penalty for this approach is about 5%. So-called "filled" resins have been used in order to reduce potting weight with no degrading effect on the seal noted to date.

3.3 KEY FACTORS IN DESIGN AND MANUFACTURE OF HERMETIC SEALS

Information was solicited from manufacturers and users regarding the factors considered most critical to the long-term integrity of hermetic seals for use in alkaline electrochemical cells. An attempt was made to separate design factors from manufacturing (i.e., processing and control) factors as far as possible. The results were not as complete as desired because vendors declined to discuss the necessary details and users generally were not familiar with the technology. Furthermore, as indicated below, responses from different sources were conflicting. An independent analysis made by the Materials and Processes Department of TRW Systems served as the basis for specific questions put to vendors. This investigation was concentrated on ceramic-to-metal seals in which the active metal hydride process is used for metallizing.

3.3.1 Design Requirements for Ceramic-to-Metal Seals

Key design requirements for ceramic-to-metal seals for any application are:

a. Proper matching of expansion coefficients should exist between metal and nonmetal mating parts.

b. A braze alloy should be used that is strong yet malleable, forms a strong bond with the metallized surface of the insulator, and does not crack in service.

c. The insulator must be under compression in all dimensions at use conditions.

d. Localized stresses in insulator and in braze should be minimized.

e. Design should facilitate manufacturing and inspection operations.

Additional design requirements for seals used in alkaline cells are:

a. Insulator and braze material must be completely inert to KOH solution in the presence of oxygen, hydrogen, and applied potentials up to +1.5 V.

b. Any new materials formed by the bonding processes must be inert.

All vendors agreed that these were valid basic requirements, but relative emphasis and methods of implementation varied considerably, as indicated by the variety of designs described above. The reasons usually given for using particular methods were that tests (by vendors) had shown the method to be adequate, and/or that complaints received were insufficient to justify the cost of improvements. No vendors offered evidence that detailed scientific analysis had been made of their seal design prior to its use in spacecraft cells.

3.3.2 Manufacturing Requirements

3.3.2.1 Process Control

The following areas of process control were identified as potentially critical and were reviewed with vendors:

a. Controlled composition of ceramic and braze materials

b. Cleanliness of surfaces and freedom from volatile substances

c. Clearance and alignment between mating metal and non-metal parts

d. Amount of hydride used, and effect of discontinuities in the hydride

e. Pressure and composition of residual gas during vacuum firing

f. Temperature profile of work during firing

g. Use of a heat-sink when cover is welded to cell case

Most vendors felt that controlled composition of materials and clean surfaces were essential to uniformly good seals, but the quantitative dependency was not known. Actual controls exerted were considered sensitive information by vendors, and although they were willing to divulge details to individual customers, they requested that such details not be published.

While one vendor indicated that improper alignment of parts, if not great, has little effect on seal quality, another vendor presented data that showed proper alignment is of extreme importance. If the mating parts are not precisely aligned, the braze joint can be thick on one side and thin on the other. Then, when the cover is welded to the case, uneven stressing of the joint occurs which can result in the start of cracks. Alignment is generally established by jigging, and is checked visually.

One vendor indicated that not enough metal hydride results in an inferior seal but that too much hydride would have little effect on the seal quality. Another vendor indicated that both too little and too much hydride result in an inferior seal, pointing out that because of the limited solubility of titanium and zirconium in the braze materials, too much hydride results in a brittle titanium or zirconium rich zone in the braze that can develop cracks. Vendors agree that small discontinuities in the hydride coating have little effect on the seal quality, as the hydride flows and wets the ceramic as the brazing temperature is reached.

Although vendors believed that the quality of the vacuum and the temperature profile during firing could have some effect on seal quality, they did not know the degree of dependence and presumably had not investigated these effects. It was therefore assumed that controls on these variables were minimal.

Some vendors have dispensed with the heat-sink while the cover is being welded to the case because, it is claimed, the use of the stress-relief collar reduces the heat and stress applied to the ceramic-to-metal joints. Low failure rates from inspection are quoted as substantiation. One vendor considers heat-sinking desirable, despite the presence of a stress-relief collar, because of potential long-term problems which can result from stresses due to any uneven thickness of the braze material.

3.3.3.2 Manufacturing Quality Control and Inspection

A survey was made of quality control and inspection methods used by manufacturers of ceramic-to-metal seals. Here again, as with process controls, details were withheld as proprietary or not for publication. It was apparent that each vendor has an established minimum level of testing that is about the same for all and that establishes the basic catalogue price of the cell. Any customer may add to this level, at additional cost.

A typical example of an inspection test specification suitable for use by a vendor on cover assemblies for spacecraft-quality nickel-cadmium cells, is shown in outline form in Table 5. For some items, the AQL level was increased to 100% from some lower value; in some cases the method of testing was changed; and in other cases, new test steps were added to the minimum plan. The resulting procedure involved 50% more labor than the original and added to the price of the cell.

3.4 CORRELATION OF SEAL PROBLEMS WITH CONFIGURATION OF NICKEL-CADMIUM CELLS

3.4.1 Cell Geometry

Of the two geometries of nickel-cadmium cells now available, prismatic and cylindrical, the prismatic configuration is most generally used for spacecraft cells. With few exceptions, companies now using cells of a cylindrical configuration are doing so primarily because the spacecraft involved was designed for cylindrical cells at a time when they were relatively more available, and redesign to accommodate prismatic cells is not cost-effective now. Certain users prefer cylindrical cells because they are more able to contain high internal pressure without need for restraining hardware to prevent deformation. Most users, including those using the cylindrical configuration, agree that prismatic cells lend themselves to higher density packaging and more efficient dissipation of heat.

The users contacted did not have an opinion as to whether cell size or configuration determines the type of seal to be used. It appears that in prismatic cells less than 1 in. thick, the limited sealing area available may reduce the effectiveness of a compression type seal. As the technology improves, this limitation may disappear. Plitt seals less than 1 in. in diameter are currently being tested on prismatic cells at NAD (Naval Ammunition Depot), Crane, Indiana. NRL (Naval Research Laboratories) prefers cylindrical cells with a diameter less than 1-1/2 in. for use with Sonotone's triple-seal because with this configuration, the cover can be made very rigid (by providing a heavy gage material) and therefore resistant to flexing with pressure variations. NRL believes that flexing of the cover is a major contributor to failure of the seal. It is believed that flexing of the cover should not be a problem with the current terminal assemblies offered by Gulton and G. E. because of the action of the stress-relief collar used.

3.4.2 One Versus Two Insulated Terminals (Prismatic Nickel-Cadmium Cells)

A small majority of users prefer one insulated terminal rather than two, based on their experience showing leaking seals to be more prevalent than internal shorting by silver migration. This position is not necessarily relevant for long-term applications; however, it is based on what has been seen during ground testing of cells over periods lasting usually less than 1 yr, during which time shorting may occur only rarely. Also, the experience referred to is largely with older cells having seals prone to leakage of obsolete design. Improvements in seal design have reduced this shorting problem.

Some users correctly point out that internally generated heat can be more easily transferred out of the cell if one set of plates is connected directly to the case. This is mainly because the outside plates in one-insulator cells are directly in contact with the cell container wall; whereas in two-insulator cells, a layer of plastic material is used to electrically insulate the plate stack from the container wall. The larger the cell, the more this difference in design may affect the internal cell operating temperature, and hence electrical performance.

A potential problem with one-insulator cells has recently come to light. If a tool is accidently placed in contact with both the terminal post and the stress-relief collar, the current that flows can be sufficient to burn a hole through the relatively thin collar before the short can be removed. This same type of external short in a two-insulator cell causes no damage, as the current that flows is insignificant (unless, of course, both insulators are shorted simultaneously).

Most of those contacted felt that two insulated terminals would reduce the incidence of silver shorting by dividing the voltage gradient per insulator in half. No proof was offered. As described in paragraph 4.2.2, tests have shown signs of silver migration within 6 mo using two-insulator designs, but the relative incidence and rates are low compared to the one-insulator configuration. Thus, the two-insulator design appears preferable.

3.4.3 Soldered Versus Threaded Terminal Connections

Most users prefer and use soldered or crimp-solder connectors for cells up to and including the 20 A-hr size. Their reasons for this choice are: (1) soldering makes a better mechanical joint which is not affected by shock and vibration, (2) less human error is involved in soldering versus torquing necessary for threaded terminals, and (3) applied torque necessary to effect good contact with threaded connections could damage the seal assembly. For cells much larger than 20 A-hr capacity, a threaded lug is preferred. Users indicated that larger size terminals associated with larger capacity cells are more suited to threaded lugs because: (1) soldering to terminals of this size is likely to result in "cold solder" joints and (2) more torque can be applied with little chance of damage to the seal assembly because the latter is larger and stronger.

Soldering lugs (attachments to the terminals intended to facilitate solder attachment of leads) are considered by most of those having experience in assembling batteries to be an advantage in that they simplify the interconnecting of cells and they reduce the amount of heat transferred to the ceramic-to-metal joint during the process. Others felt that the probability of damage to the seal by heating during direct soldering to the terminal post was small and could be minimized by carefully specifying and supervising soldering techniques. The material and finish of the lug should be specified. Untinned copper lugs can lead to contamination of the insulator and other surfaces at the top of the cell.

Table 5. Typical Inspection Test Specification Pertaining to the Cell Cover Assembly

I. Materials Inspection

A. Every shipment of raw materials received shall be inspected as follows:

1. Select sample at random (AQL 1%)

2. From above sample, select five pieces and inspect for all attributes

3. If five pieces are good, inspect rest of sample for all attributes

4. If the number of defects found in the five pieces equals one or more, reject the lot

II. Cover Assembly

A. Weld pinch tube to cover

1. Inspect (100%) weld for:

a) Cracks

b) Porosity

c) Folds

d) Excessively oxidized metal

e) Finished weld shall be free of discoloration and foreign matter

f) Maximum allowed variation in weld surface (peaks-to-crater)

III. Assembly of Cover

A. Inspect (100% visually) hydride coating on ceramic for holes and evenness of coating

B. Inspect (100% visually) ceramic and cover hole for nicks, chips, or deep scratches

C. Assemble cover, hydride coated ceramic, and braze rings in positioning jig and inspect (100% visually) for alignment of parts

Table 5. Typical Inspection Test Specification Pertaining to the Cell Cover Assembly (Continued)

IV. Inspection of Cover Assembly After Firing

A. Visually inspect (100%) seal junction for continuity on top and bottom per specimen standards

B. Check (100%) terminal location per drawing

C. Helium leak test (100%); leak rate shall not exceed 1×10^{-8} cc/sec

D. Verify helium leak test (recheck 1 out of 12)

E. Insulator resistance test (100%)

F. Inspect exposed braze surfaces (100%) under 10 x magnification for:

1. Continuity of braze joint

2. Flowout of braze joint (limits per specification)

3. Depressions of braze joint (limits per specification)

4. Pinholes in braze joint (limits per specification)

V. Inspection of Plating Facility

A. Inspection

1. Incoming material: check for count and any discrepancies

2. After hydrohoning, each header inspected for contamination, foreign matter embedded in braze or ceramic

3. Check (100%) thickness of Ni plate with Magnagauge

4. Check (100%) Ni plate for adhesion (tape test), lifting, blisters, etc.

Table 5. Typical Inspection Test Specification Pertaining to the Cell Cover Assembly (Continued)

B. Quality Control

1. Magnagauge checked weekly against standard

2. All solutions analyzed weekly

3. Temperature devices checked against standard semiannually

4. Ammeters and voltmeters on rectifier checked against standards semiannually

VI. Inspection of Plated Headers After Return to Vendor

A. Visually inspect (100%) for completeness of plating

B. Helium leak test (100%) (leak rate shall not exceed 1×10^{-8} cc/sec)

C. Verify helium leak test (recheck 1 out of 12)

D. Insulator resistance test (100%)

VII. After Completing Assembly of Cell

A. X-ray photograph (100%)

1. Visually inspect photographs for voids in terminal braze joints

B. Electrolyte leakage test (100%)

1. Apply phenolphthalein solution to all welds and braze joints, and visually check for red color

C. Helium leak test (100%)

1. Helium leak rate shall not exceed 10^{-7} atm cc/sec

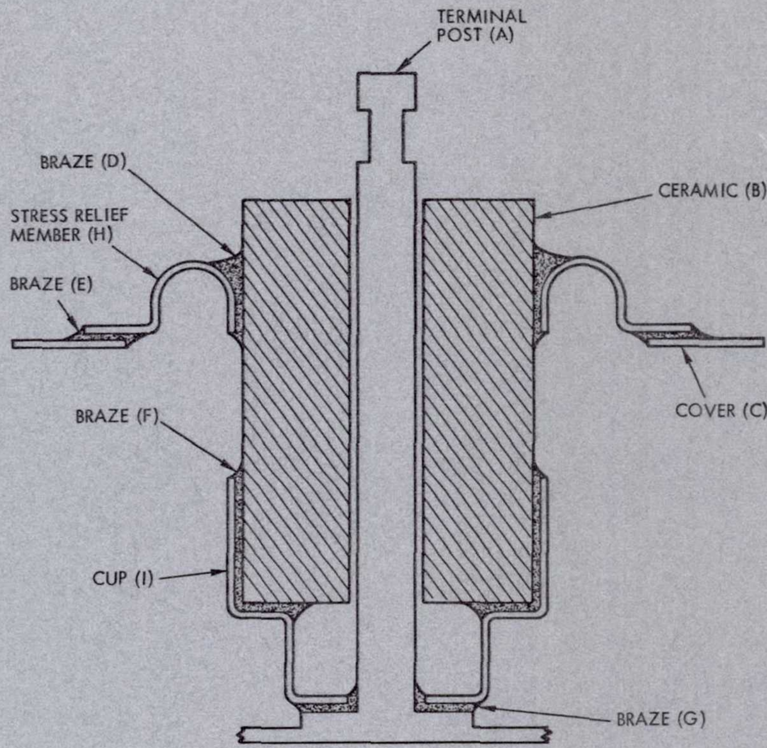

Figure 1. Gulton Ceramic-to-Metal Terminal Seal

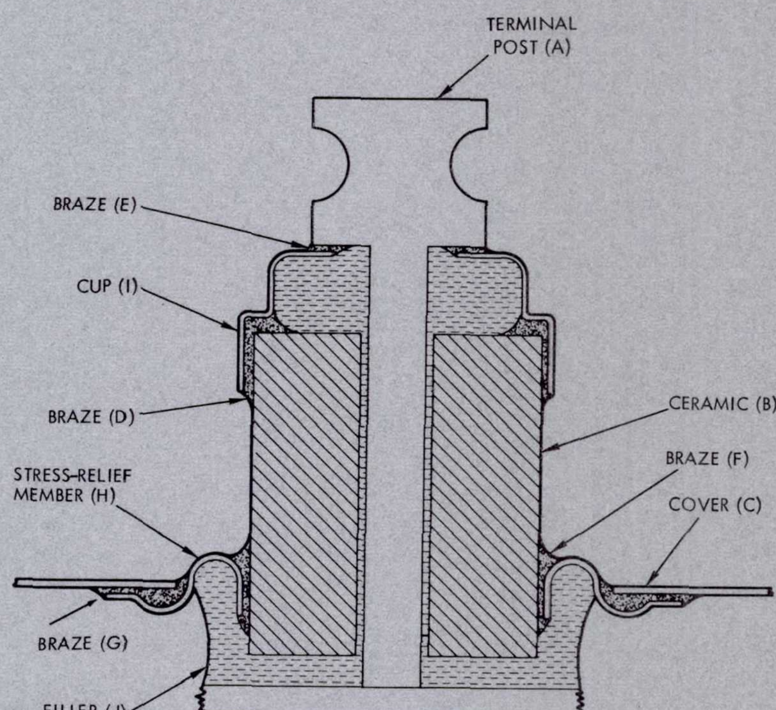

Figure 2. General Electric Ceramic-to-Metal Terminal Seal

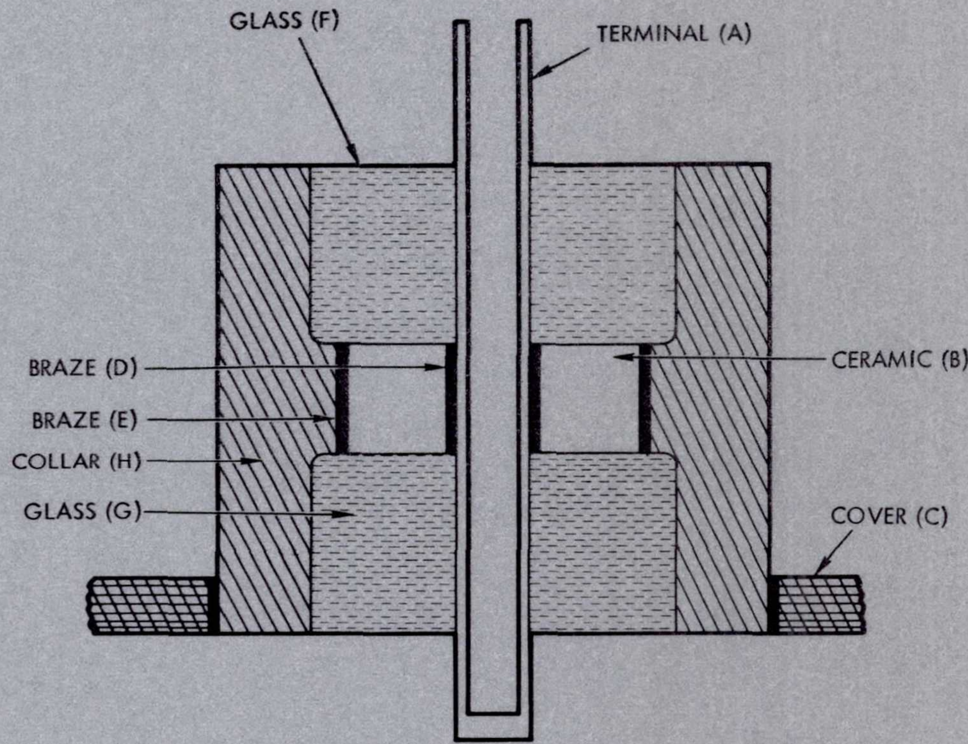

Figure 3. Sonotone Triple-Seal

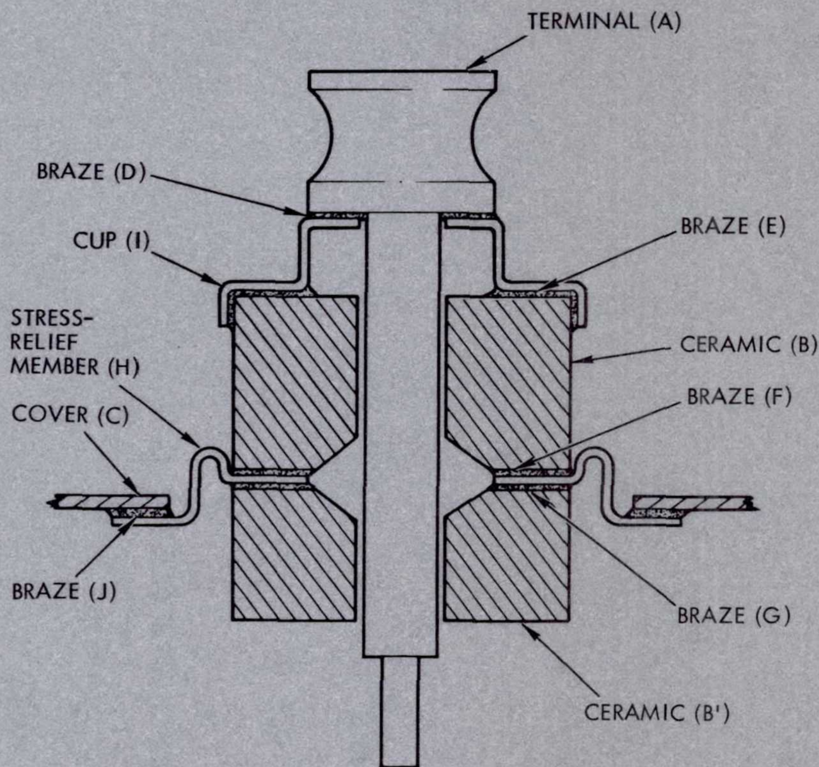

Figure 4. Experimental General Electric Ceramic-to-Metal Terminal Seal

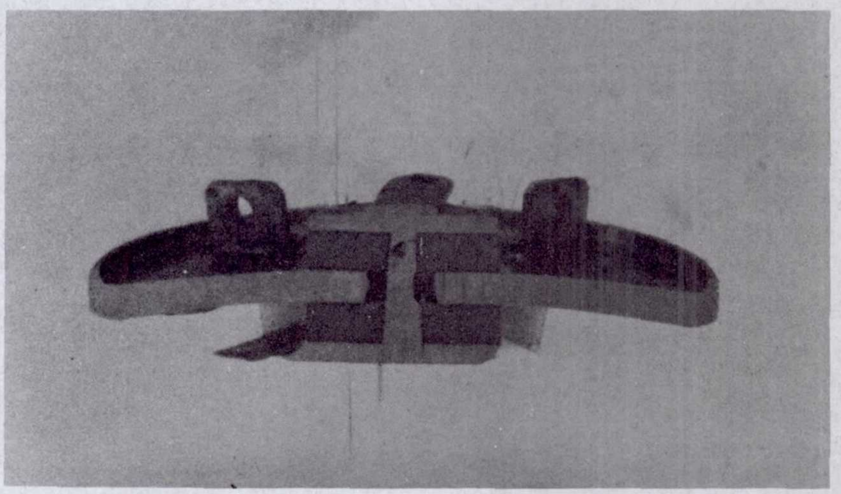

Figure 5. Experimental RCA Ceramic-to-Metal Terminal Seal

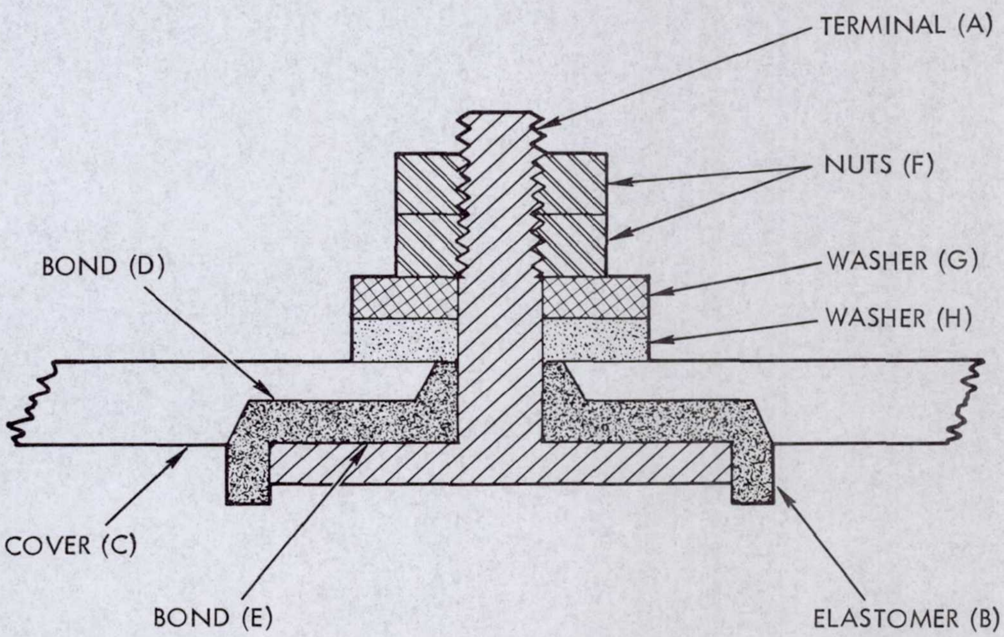

Figure 6. Plitt Compression Seal

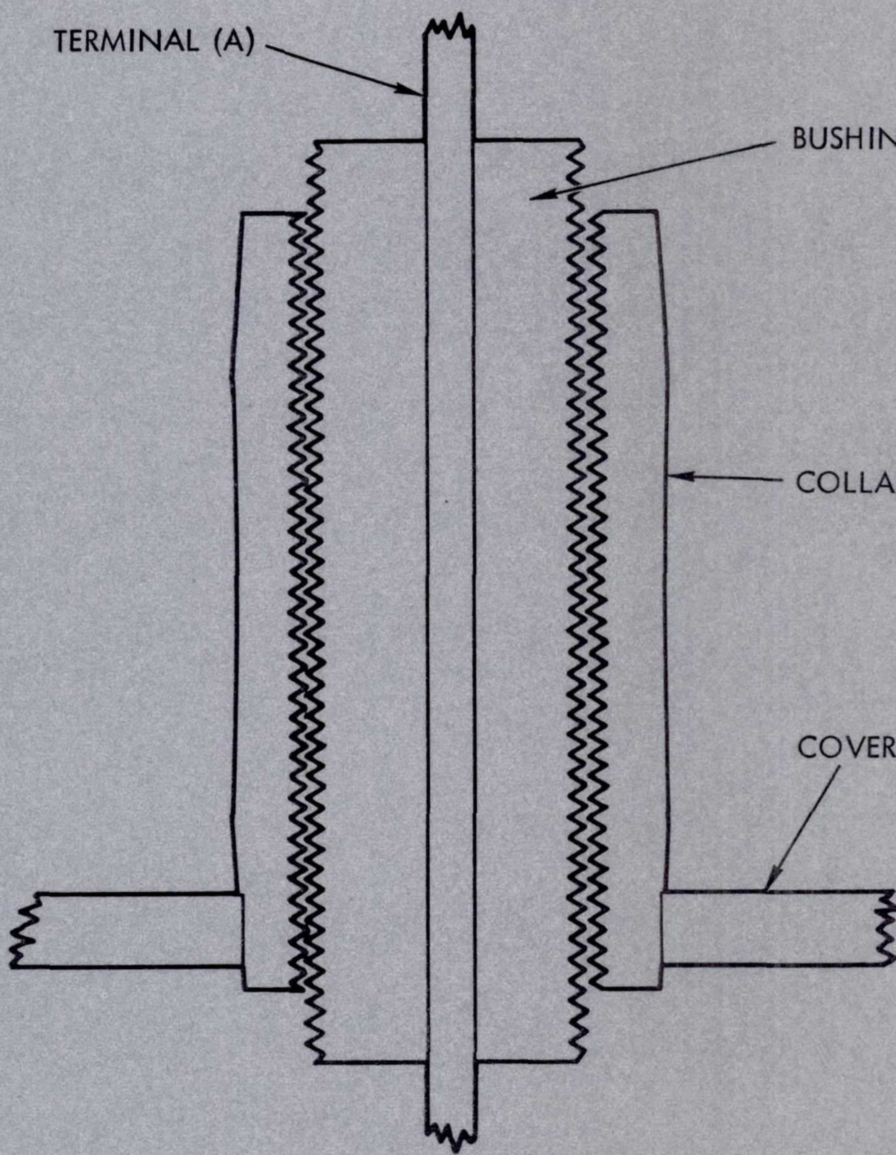

Figure 7. Ziegler Compression Seal

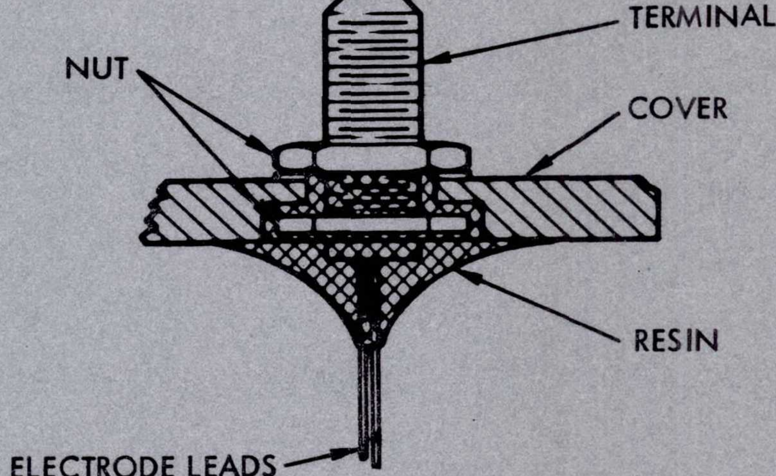

Figure 8. Standard Integral Plastic-to-Metal Terminal Seal

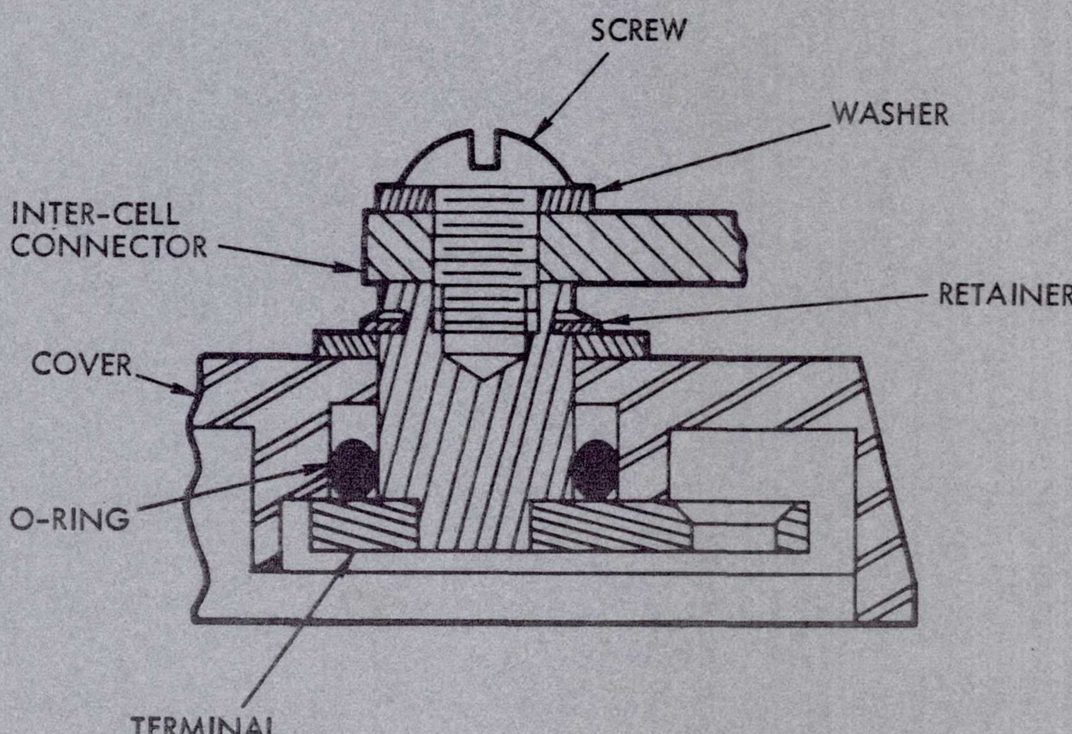

Figure 9. User-Developed Integral Plastic-to-Metal Terminal Seal

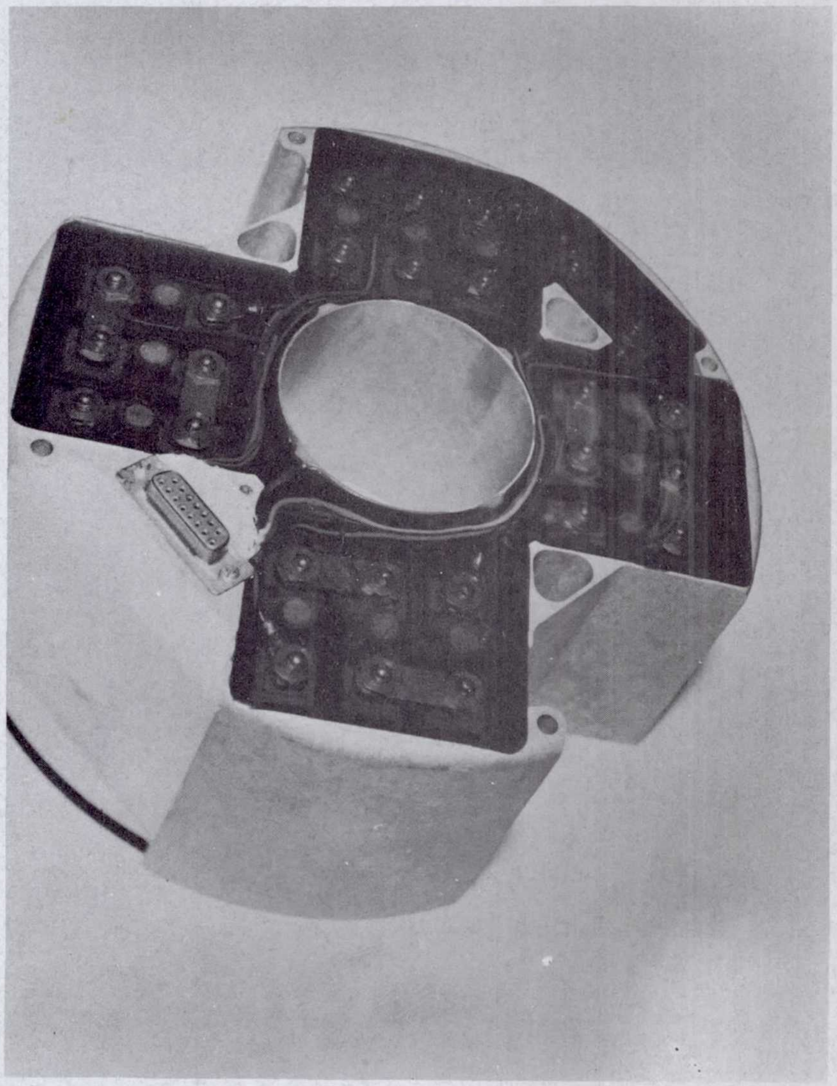

Figure 10. Potted Overall Battery Seal

4. FAILURE MODES, TEST METHODS, AND TEST RESULTS

This section presents the important failure modes of sealed spacecraft cells, suggests mechanisms of failure, and describes test methods used and results obtained on state-of-the-art terminal seals.

4.1 SEAL FAILURE MODES AND MECHANISMS

By far the most frequently occurring failure modes of seals on alkaline cells are slow leakage and, for ceramic-to-metal seals, shorting across the insulator. These are also the least understood. The more drastic types of failures, such as gross mechanical breakage or rupture due to high internal cell pressure, occur only rarely and are not discussed here.

4.1.1 Failure by Leakage

4.1.1.1 Nickel-Cadmium Cells

Leakage from a ceramic-to-metal seal has been observed to occur through a crack in the ceramic, through a crack in the braze, through a hole in the braze, or through a discontinuity in the ceramic-braze interface. Each of these leakage paths results from different causes. A cracked ceramic results from stressing the material beyond its limit. The total stress is the sum of residual stresses produced by the effect of difference of properties between the ceramic and the braze material, and applied stresses produced by relative motion between the cell case and the plate stack. Figures 11 and 12 are photographs showing two cracked insulators after sectioning and polishing. In Figure 11 the crack runs parallel to the surface of the insulator for the length of the braze; in Figure 12 the crack is hemispherical. In other cases, the crack goes through the insulator in a plane perpendicular to the axis of the terminal.

Cracks wholly within the braze material, which occur much less frequently, often result from phase separation of the alloy, a process which greatly reduces the rupture strength. This type of failure occurs primarily with noneutectic alloys.

Holes in the braze are distinguished from cracks in that the former are present as a result of incomplete flow or wetting and/or effects of inclusion of foreign material. A photograph of a sectioned terminal showing a void in the braze is shown in Figure 13. Such voids appear to be the type that occur during the brazing operation of manufacturing. The void shown was not continuous through the braze, and hence, by itself, was not responsible for the leak. This terminal did not leak for some time after completion of the cell, but in conjunction with the action of KOH on the interface (see below), the void contributed to leakage early in life.

It is believed that the most frequently occurring leakage path is the interface between the ceramic and the braze. Statistics are not available because very few leaking terminals have been analyzed to determine how and why the leak occurs. The following mechanism is therefore proposed without proof.

When the ceramic surface becomes metallized, chemical bonds are formed between the metal and the alumina. These bonds are believed to form primarily between metal and oxygen atoms, and result in the formation of a complex glassy layer at the metal-ceramic interface. Hence, new compounds are formed that may have much higher solubility in KOH solution than any of the starting materials. The solubility of this interface material may be further increased because the material is under residual stress and thus is in a higher energy state than normal. Residual stress results from the fact that the bond is formed at high temperature and then cooled to ambient temperature for use. The cooling causes the metal parts to contract more than the ceramic, with the braze having to accommodate the relative charge in dimensions. This is why a braze material must be malleable to perform satisfactorily in this application.

A few users have observed alkaline leakage primarily at the negative terminal or on the relatively negative side of the insulator in a one-insulator type cell. Others have seen no such orientation. Records were not available to show whether this behavior correlated with cell type or manufacturer. No satisfactory explanation for negative-oriented leakage has been forthcoming.

The unusual surface activity of aqueous KOH undoubtedly aids in the penetration of the insulator-to-metal interface. The ability of KOH to creep is well known to chemists. Creep describes a process whereby KOH migrates out of solutions and covers adjacent surfaces with a thin film, bringing water with it. The driving force is the lower energy state of the wetted surfaces. Creepage provides a process whereby the inner surfaces of the terminal seals in a cell may come in contact with KOH solution even though the cell is starved, i. e., contains no free electrolyte solution.

Failure by leakage of compression-type seals on nickel-cadmium cells may occur by self-decomposition of the bond between the gaskets and the metal parts, by chemical attack on the bond by KOH and/or oxygen in the cell, or by physical penetration of the gasket-to-metal interface via voids in the bond. Any or all of these mechanisms may operate together, assisted by shrinkage or hardening of the gasket material.

4.1.1.2 Leakage in Silver-Cadmium and Silver-Zinc Cells

Leakage at the terminal seal of silver-cadmium and silver-zinc cells is the only seal failure mode observed with the cells (other than gross breakage). Leakage occurs either through the metal-to-plastic (cement) interface or through cracks in the insulating material surrounding the terminals. Leakage through the interface occurs either because of incomplete bonding during fabrication, or loss of complete bonding due to physical forces or chemical attack by the contents of the cell.

Cracking or crazing of the plastic around the terminals occurs because of excessive stresses or the action of certain solvents used to facilitate the plastic-to-metal bonding process. JPL has found that the age of the plastic cell case material affects the tendency toward crazing. Cases less than 2 years old show little if any crazing, while those over 3 years old craze easily. Certain solvents, such as methylene chloride, commonly used to clean and process plastic-to-metal and plastic-to-plastic seals, cause excessive crazing. Other solvents that do not cause this problem usually can be substituted.

4.1.2 Failure by Shorting Across the Insulator

The second major failure mode of terminal seal assemblies involving ceramic-to-metal seals is that of shorting of the insulator, which effectively shorts the cell. The only significant form of shorting observed is that occurring inside the cell and, in every case investigated, it is due to a deposit of silver bridging the insulator. Such deposits are always associated with a braze material containing silver; no shorting has been observed when silver is not used in fabrication of the seal assembly.

The mechanism of this process has not been demonstrated, but the following theory appears reasonable. In the presence of aqueous KOH and a potential difference across the insulator, silver in the braze is oxidized at the positive side and diffuses through the liquid film on the ceramic surface in the form of a soluble ion. Silver is reduced to the metallic state at the negative side of the insulator and, under suitable conditions, forms an adherent deposit. This deposit can form a continuous path from the positive to the negative side, having sufficiently low resistance to interfere with the operation of the cell. Several stages of this process are illustrated in Figures 14 through 16. The terminal in this case was made by using a pure silver braze, nickel plated. Exposure was to air, over KOH solution, with 1.45 V across the insulator.

The specific conditions (other than those of the general environment inside the cell) necessary for the formation of a low-resistance short are not known at this time. It is known that bridging does not occur when no potential difference is applied across the insulator, but it is not known how high a voltage is required. One of the arguments in favor of the use of two insulated terminals instead of one is that the potential across each insulator is then about half that across the insulator of a one-insulator cell, and thus silver migration may be suppressed. Results of recent tests at TRW on two-insulator cells indicate that, although migration may be slower, it still occurs with this configuration.

For some time, Gulton has applied a nickel plating over the braze in their seal to mitigate the silver-migration problem. Nickel plating does reduce both the incidence and the rate of silver migration from silver-containing brazes during the first year of life. Plating over pure silver did not appear to be a long-term solution, however, as indicated by the results of a 6-mo exposure test (Figure 17). Although the plating was probably adequate where it was pore-free and adherent, the latter requirements proved difficult to satisfy. Figure 17 shows the plating peeled off a terminal after a period of testing in an operational cell.

In a subsequent improvement, Gulton changed to a copper-silver alloy braze material and, at the same time, introduced a stress-relief collar in their design (shown in Figure 1). The copper-silver alloy had been shown by work in other fields to be much less susceptible to silver migration; in addition, it accomplished better alloying with the metal parts used for the terminal assembly. Corrosion tests in KOH produced considerable blackening and contamination; hence, the nickel plating was retained on the improved terminal. The limitations of the nickel plate can be expected to be the same as those discussed above, so that the long-term resistance to silver migration will depend largely on the inherent properties of the braze alloy. Tests of the state-of-the-art Gulton terminals at TRW have shown some silver migration, but no shorting of the insulator has been observed to date at TRW or by other users either in simulation tests or in complete cells.

Analysis shows that the shorting failure mode for the G. E. terminal is possible but less probable than for the Gulton terminal. The braze material used is a copper-silver alloy and, as indicated in Figure 12, the distance along the insulator surface from the inner surface of one ceramic-to-metal braze (such as D) to the closest inner surface operating at a different voltage level (either more positive or more negative, depending on which terminal is considered) is relatively long, such as to braze F. Also, the intervening space is filled with an epoxy resin in the standard design.

These protective features can fail, however. If the terminal is on the negative side, braze F is positive to the post and, therefore, unless the post is well centered in the hole in the insulator, it may touch at the bottom end, providing a relatively negative electrode close to the inner surface of braze F. Silver would then have to traverse only the bottom end of the ceramic to cause shorting.

A completely adherent epoxy coating would prevent this, but it has been demonstrated that KOH solution is capable of penetrating between the epoxy resin coatings and various substrates tested to date. The degree of penetration of the bond required to promote silver migration and the conditions under which this penetration occurs are not known. In one test at TRW a black deposit was seen growing across the insulator under the epoxy layer, but electrical shorting did not occur. Only a few cases of shorting at the terminal of G.E. cells were found during this study.

Silver-cadmium and silver-zinc cells are not subject to shorting at the insulator since all-plastic cases are used. Another form of silver shorting does occur in these cells, however, and is caused by silver migration through and around the separators. Although the effect on the cell performance is ultimately the same, the location and mechanism of it is different from that in nickel-cadmium cells. A study of this failure mode is beyond the scope of this work.

4.2 QUALIFICATION TESTING OF TERMINAL SEALS

This section describes qualification test methods currently used to demonstrate the ability of a terminal seal to meet certain requirements. Tests conducted by cell vendors are differentiated from those conducted by users; test results are presented in subsection 4.6.

4.2.1 Test Methods Used by Cell Vendors

Tests are conducted both on cover assemblies alone and on complete cells. The tests run on cover assemblies alone are of two types: mechanical and electrochemical. Mechanical tests include vibration, flexing, shock, and rupture strength. Visual inspection and helium leak measurements are used to determine the results. Electrochemical testing (also referred to as corrosion testing) has been done both under normal conditions and also under conditions intended to provide a high stress level and thus accelerate failure. A typical electrochemical test for a ceramic-to-metal seal under mild conditions consists of immersing seal assemblies in 32% KOH solution and/or suspending the samples above the KOH solution at room temperature, while applying a voltage cycled between 1 and 1.5 V across the insulators. Samples are removed at intervals, inspected visually, checked for helium leak rate, and measured for resistance across the insulator. Total test time varies from 30 to 90 days. If a new seal passes this test, it may be incorporated into the standard line of cells without further testing.

In order to accelerate these tests, some experimentation has been done with the conditions, e.g., temperatures up to 120°C, applied voltages up to 1.75 V, and rapid voltage cycling or voltage pulsing, i.e., on and off at frequencies of once every few minutes. Marked increases in degradation rates are observed under these conditions, especially when used in combination. No data or other information were offered to indicate how the results from these tests correlate with experience in the real cell environment. The accelerated tests were used primarily for comparing the performance of different terminal designs during development.

In addition to the above tests, extended life testing of seals in actual cells is usually carried out by vendors. A group of test cells are cycled continually, and at intervals one or more cells are removed from cycling and are torn down. Visual inspection and electrical resistance across the insulation are used to determine the condition of the seal assembly. Mechanical tests are not normally repeated so that the effect of aging on strength is not known.

4.2.2 Test Methods Used by Cell Users and Test Organizations

Testing by users falls into several categories, each providing a different kind of information on hermetic seals. These include: (1) testing terminal seals outside of complete cells, (2) acceptance testing of complete cells for either further ground testing or for assembly of cells into flight batteries, and (3) life cycle testing on the ground. Space flight itself is not considered a test, but it does provide a source of confirmatory data which was considered in this study.

The survey revealed that no users of nickel-cadmium cells other than TRW had done any significant testing on terminal seals other than observing their behavior in complete cells. The general opinion was that, in the absence of an understanding of the failure mechanisms and with no accepted test methods available other than those involving the whole cell, tests on separate terminals would not be productive. Recognizing this problem, TRW has been conducting an experimental test program during the last 2 yr. Both accelerated and nonaccelerated test methods have been explored. This effort has been directed at methods that can be used on cell covers and seal assemblies not attached to cell cases in order to reduce test costs and to allow continuous visual observation during testing.

Accelerated methods tried were essentially the same as those used by vendors, which were previously described. Results have been erratic and unreliable. A more meaningful test currently in progress is a longer term one, and consists of the following conditions:

a. Immersion of the underside of the cell cover assemblies in an atmosphere consisting of pure oxygen at 1 atm and a relative humidity regulated by a reservoir of 32% aqueous KOH

b. Wetting of the surfaces of the seals with 32% KOH when the specimens are first placed on test, with no further manual wetting

c. Application of voltage cycled between 1.0 and 1.5 V between the terminal and the cover or between the two terminals, depending on whether one or two insulators are involved

d. Operation at room temperature

It is not yet known how these results correlate with field experience since the cells with the tested terminals have not been in service long enough. This type of test, requiring 6 months or more, is difficult to fit into regular hardware schedules so that an accelerated test is still needed.

Testing of complete cells by users is performed primarily to determine the electrical response of the cells. Acceptance tests are necessarily brief and thus can reveal only those deficiencies that show themselves within a period of about six months or less after manufacture. Life cycle tests may continue for years, and thus should demonstrate long-term random failures and wear-out. Life testing usually is conducted on cells that have passed acceptance and matching tests, with the purpose of screening out very early failures. This is not always successful, as indicated by the high failure rate during the early stages of cycle tests on some cells in the NASA program at NAD, Crane.

No cell tests are made by users or testers solely to test the terminal seal. Because of this and the difficulties of leak testing, the condition of the seals usually has not been recorded until a cell fails by electrical malfunction. Therefore, these cell tests although involving the largest number of samples in any test category, produced relatively little seal test data useful to this study.

The methods used for acceptance and cycle testing of cells vary considerably from user to user, and are not all reproduced here. Test conditions can strongly affect seal failure rates, e.g., seal failures will be more frequent at high temperature and/or when combinations of charge rate and charge voltage limit permit high pressure to accumulate in the cells.

Certain test methods directed at the seals, common to all cell test programs, are discussed in the following sections.

4.3 LEAK TESTING

The two leak tests most frequently used for determining the hermeticity of a seal are the alkaline leak test and the helium gas leak test. The two tests are related to the two different types of leaks which, as pointed out earlier, can occur independently.

4.3.1 Alkaline Leak Testing

Details of alkaline leak testing vary from vendor to vendor and from user to user. Organic, acid-base indicators, such as phenolphthalein, cresol red, bromthymol blue, "Vivid 1-11," and litmus paper, are used. Also, different concentrations of the same indicator are used; different methods are used to apply the indicator solution to the terminals; and different contact times for the application of indicator are used.

Some of the methods of application being used are the following: (1) immersing the cell in indicator solution, (2) applying indicator solution via cotton swabs, (3) applying solution by spraying, and (4) applying wet litmus paper to the terminals. Times of contact vary between a few seconds to 15 minutes. The net effect of these variations in technique is a wide range of detection sensitivity and reliability.

The time allowed for contact is considered critical. Cells are often washed prior to alkaline leak testing. Such washing removes any surface accumulation of alkaline material, leaving whatever may be in the pores and crevices. Material in the pores requires some time to diffuse to the point where a clear-cut color indicator reaction may be seen. A few seconds is not enough time; 30 seconds may not be sufficient time for reliable detection of a slow leak. Some argue that contact beyond a few seconds allows the water usually present in the indicator solution to begin to electrolyze, producing an alkaline solution at the negative side of the insulator and hence giving a false leak test. In addition, longer standing can permit volatile solvents, including water, to evaporate, possibly changing the nature of the color reaction. These are valid points, but they do not justify negating the test with a very short contact time.

One way to avoid electrolysis of the test solution is to test only when the cell is completely discharged and shorted. This approach is considered unduly restrictive; in addition, it is desirable to be able to test for alkaline leakage while cells are being overcharged, since leakage may be accelerated in this condition by the effect of oxygen pressure within the cell.

Another approach to this problem, currently under evaluation at TRW, is the use of a nonaqueous test solution. Solutions of phenolphthalein in mixtures of organic solvents have been found to have a high sensitivity to the external deposits formed by cell leakage; they retain their liquid condition for long periods depending on the solvents chosen; and they do not electrolyze at the voltage of a charged cell. The use of a nonaqueous solution has the additional advantage of not leaving water in contact with the termal seal surfaces subject to corrosion. For the same reason, the test solution should be washed off the cell with a nonaqueous solvent.

The indicator should not change color at a pH less than 8, or else various contaminants, including cigarette ash, will give a positive test. A potential problem is created by the fact that CO_2 in the air begins to react with KOH as it issues from a leak, thereby reducing the pH of the deposit. Experience shows, however, that given sufficient contact time, a sensitive indicator that turns at pH 8 or above will detect any appreciable leak.

One disadvantage of the alkaline leak test is that the test may miss a leaking cell since a leak can vent gas without venting KOH. Such a situation has rarely been observed, however, the opposite has been known to occur many times. Alkaline testing may fail to detect a leak if acid flux has been left on the braze area or if acid is used to wash the terminal prior to testing. Alkaline cleaners can give a false positive test; therefore, only neutral cleaning agents should be used.

4.3.2 Gas Leak Testing

Gas leak detection is made possible by putting a minor fraction of helium in the cell during manufacture. Methods for helium gas leak testing are more uniform than those for alkaline leak testing, because of the nature of the test and the commonality of the test equipment available. The main variability in this method is the true sensitivity of the test equipment. Modern instruments in proper working order are supposed to detect 10^{-9} atm cc helium per second, but this may degrade to 10^{-8} in practice.

The disadvantages of the helium leak test include the following: the method is cumbersome to implement on completed cells; it is particularly awkward after cells have been assembled into batteries; and its reliability is reduced by the possibility that all the helium can diffuse out of the cell prior to the time the test is made. Because of this uncertainty, some users do no helium leak testing after the cells are more than a few weeks old.

Another method for gas leak detection that does not depend on the presence of any specific gas in the cell is the bubble test.* In this method the cells are immersed in a liquid, the pressure reduced, and the cell observed for gas bubbles. The disadvantages of this method are that: (1) it is much less sensitive than the helium leak test, the estimated threshold being only about 10^{-3} cc/sec and (2) it is not adaptable to testing of cells after assembly into batteries.

*See Reference, 5.

4.4 SHORT TESTING

Insulators are tested for shorting by means of electrical resistance measurements during cell manufacture prior to addition of electrolyte. Once electrolyte has been added, the insulation resistance cannot be measured directly as the low-resistance electrolyte path between the plates is then in parallel with the insulator(s).

An indirect test is used by most vendors and users to detect the presence of an internal short. After shorting down the cell externally, the cell is given a brief charge (usually at the C/10 rate of 5 min) and then allowed to stand on open circuit for 24 hr. A voltage less than 1.16 V at this time is taken to indicate an internal short. This test cannot distinguish between a short across the insulator and one between the plates, nor can it distinguish between a short and other processes that reduce cell voltage, such as chemical self discharge. For this reason the test is considered of doubtful value by some, although few cells that do not pass such a test are flown.

4.5 SEAL FAILURE ANALYSIS

Failure analysis on seals rarely has been conducted either by cell vendors or by users. What has been done to investigate leaking seals has involved metallographic sectioning and polishing followed by photographic analysis. Considerable difficulty usually is experienced in finding the leak path by this procedure. If the leak is large enough, finding the point of leakage can be facilitated by immersing the lower end of the terminal assembly (removed from the cell) in electrolyte solution with phenolphthalein indicator added, then observing the appearance of red color at the upper end. Once the path has been localized or is suspected, electron microprobe analysis can be used to aid in identifying the composition of the materials present.

Suspected shorted terminal insulators are checked by opening the cell, removing the separator from between the plates and/or cutting the plates off the terminals, and then measuring the ohmic resistance across the insulator. The location of the shorting path across the insulator usually is clearly visible. The true composition of the material deposited on the insulator has not been established to date because only minute quantities have been available for analysis and because the samples analyzed have consisted of mixtures. X-ray diffraction analysis of material scraped off terminals bearing silver braze joints has shown the presence of mainly silver, potassium as potassium carbonate, and aluminum (from the alumina insulator), as well as minor amounts of many other metals.

4.6 SEAL TEST DATA AND EXPERIENCE

Seal test data, failure frequency, and failure rate information for hermetic seals on spacecraft cells were collected and studied. This effort encountered several difficulties. First, few records have been kept of seal failures as separate from electrical cell failures. Second, the existence of a failed seal in the absence of a visible deposit due to an alkaline leak often goes undetected until or unless the electrical performance degrades. By that time the helium originally present can have been lost from the cell, resulting in a negative test for gas leakage. Third, the existence of an internal short across the insulator cannot be detected during continuous cycling at moderate charge and discharge rates unless the shorting resistance becomes less than a few ohms. Even then, a terminal short cannot be distinguished from a plate-to-plate or plate-to-can short without opening and disassembling the cell. With the exception of the NASA test program at the Quality Evaluation Laboratory, NAD, Crane, very few failure analyses have been performed. Finally, during the past few years some cell vendors have changed one or more key features of their seal designs, making the older seals, on which most history is available, obsolete. Thus in most cases the information derived for seal performance was necessarily qualitative.

4.6.1 Test Results on Ceramic-to-Metal Seals

Most testing of nickel-cadmium cells with ceramic-to-metal seals involved cells manufactured by either Gulton or General Electric and data for these tests are considered most reliable. Information from other vendors' cells of this type, such as those from Sonotone and Eagle-Picher, was relatively meager. Because the history of seals from different manufacturers differs significantly, data for the various seals are separated.

Historically, cells offered by Gulton about 5 years ago, in which unplated silver braze was used in the seals, showed about 10% seal failures during acceptance testing in one-insulator cells (the 6 A-hr size) and about 2% in two-insulator cells (the 12 A-hr size). The failures included both shorting and leaking, but not often on the same cell. An additional 10% seal failure occurred during subsequent life cycle testing during the first year on one-insulator cells, largely by shorting across the insulator. An additional 1% leakers were seen on cycle testing of two-insulator types. Insulator shorting was less than 0.1% on two-insulator cells.

Qualification tests (see paragraph 4.2.1) were conducted 2 years ago by Gulton on unincorporated cover assemblies of their current design. No leakers (leak rate greater than 10^{-9} atm cc helium per sec) or shorting (resistance less than 10^{6} ohms across a clean dry insulator) were observed after a 90-day corrosion test on six samples.

Life cycle tests on cells equipped with this header, at a temperature of 90°F, were conducted for over a year with periodic removal of cells for internal inspection. Gulton claims that no leakers or shorted terminals were found, although some darkening of the insulators was observed visually.

A test of current Gulton cell cover assemblies (not enclosed by cell cases) in a simulated cell atmosphere has been in progress for a period of 9 months at TRW. (The test conditions are described in paragraph 4.2.2.) The results of this test are as follows:

a. Deposits could be seen growing from the braze areas within 60 days after test start. Deposits were of two forms: one light colored and crystalline, the other a thin black film on the ceramic.

b. No complete bridging of the insulators has been observed visually to date. This correlates with the fact that no significant decrease in resistance across the insulators has been measured electrically.

c. Visually observed deposits occur randomly; many terminals have no deposits at all. Over 50% of the samples show some visible signs of chemical activity. Visible activity began on some samples only after 3 to 6 months of exposure.

d. These test conditions produce a much higher percentage of visual effects than testing with the terminals immersed in KOH solution. The latter condition is not representative of the cell environment and can give misleading results.

User experience to date with cells bearing the current Gulton terminal seals indicates less than a 1% frequency of alkaline leakage and no shorting during acceptance test operations. The cells to which this figure applies include 500 of the two-insulator type (9 A-hr and 12 A-hr prismatic cells) processed at TRW and over 200 of the one-insulator type (6 A-hr and 20 A-hr sizes) at NAD, Crane and at Grumman Aircraft. Relatively few of these cells have been subjected to life cycle testing so far. During such tests, alkaline leakage has occurred at about 1% per year; no insulator shorts have been detected. No significant helium leak test data have been generated. The longest test to date has been 18 months.

The terminal seal offered by General Electric on their nickel-cadmium cells has been the same for the last 4 yr, hence all test data obtained over this period are applicable to the current seal. Qualification testing originally conducted by G. E. on unincorporated cover assemblies showed helium leakage less than 10^{-9} atm cc/sec and no shorting after a 90-day corrosion test. Here again some staining of the insulator under the epoxy coating was observed. A similar test made in 1964 at TRW produced a black deposit on one sample terminal insulator under the coating, but no shorting over a 90-day period.

A total of over 200 G. E. cells have been tested at NAD, Crane since that program started in December 1963. Among those cells on which failure analysis was performed up until December 1966, there were 12 with deposits on the terminals (indicating alkaline leakage) out of a total of 120 3 A-hr cylindrical cells starting the test. These had one insulated terminal.

There were four cells with deposits out of a total of 60 12 A-hr prismatic cells starting the test. Gas leak rates were not determined, and it was not known whether the leak contributed to the cell failure. Average time to failure was about 1 year for the 3 A-hr cells and about 2 years for the 12 A-hr cells. No shorted insulators were observed. Updated data through 1967 for G. E. cells show no insulator shorting during that period. Alkaline leakers have not been recorded. No new G. E. cells have been put on test at NAD, Crane since 1965.

The Sonotone triple-seal has been available only on cylindrical cells to date (although prismatic cells with this seal are now available on special order). Tests at NAD, Crane show two cells having alkaline deposits out of 30 cells on test from July 1965 to December 1967. NRL, Washington, reports very few alkaline leakers out of several hundred cells processed, but no extended life testing has been run. No shorted insulators have been observed, but several cases of cracking of one of the glass seals have occurred.

4.6.2 Test Results on Rubber and Compression Seals

Most test data and observations on rubber and/or compression seals come from the NASA program at NAD, Crane, since these seals are not yet qualified for space flight. A few users have obtained pilot quantities of the associated cells for test.

Several different configurations of rubber seals have been tested at NAD, Crane for extended periods. Non-folded and folded designs were fabricated using cylindrical cell containers. Complete evaluation of these designs was prevented by the occurrence of leakage at the cover weld in many test cells. This problem was shown to be due to the fact that the cells were made without the use of a fill tube, and hence electrolyte had to be added before welding the cover. Contact of the metal surfaces with KOH solution resulted in poor welds. Considerable leakage at the rubber seals also has been observed.

More recent, improved rubber seals, tested on both cylindrical and prismatic cells, are more promising. The Plitt seal (see paragraph 3.1.2.2) has been on test in cylindrical cells for 16 mo with one leaker out of 35 cells observed to date. Tests recently have been begun on a group of prismatic cells with Plitt seals. A somewhat similar design, in which positive compression is maintained by spring tension, has resulted in some leakage during acceptance testing, and is not yet on cycle test.

No testing of nonelastic compression seals is now in progress. Experience with nylon washer seals in the past has shown them to be unreliable, and no further development work was encountered for space application. The Ziegler seal, on the other hand, has been tested at the Bell Telephone Laboratories. Small cylindrical cells equipped with this seal were continuously overcharged at the C/10 rate for 5 yr at room temperature with no visible leakage at the seals.

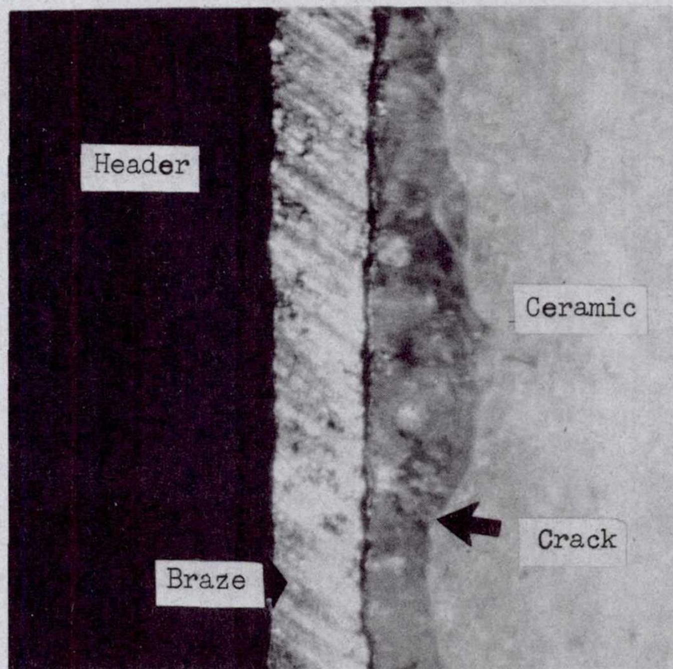

Figure 11. Section of Ceramic-to-Metal Seal Showing Crack in Ceramic Parallel to Braze Surface

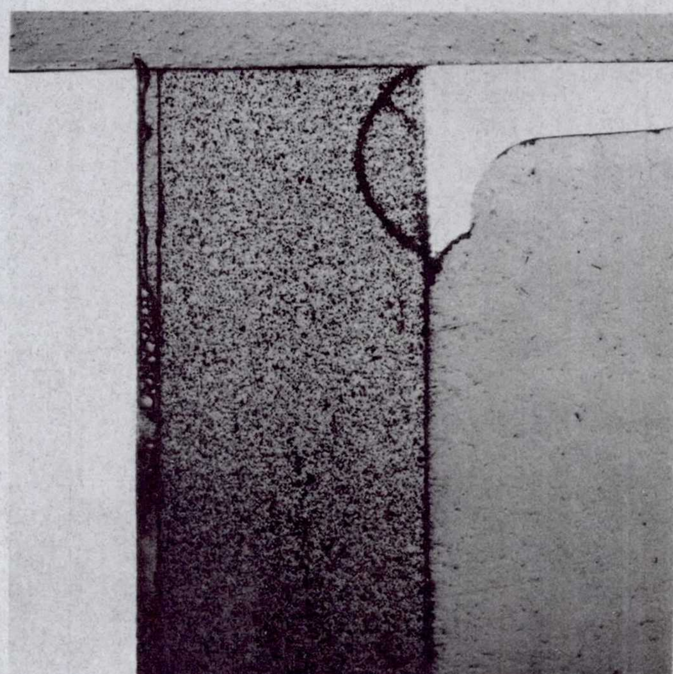

Figure 12. Section of Ceramic-to-Metal Seal Showing Hemispherical Crack in Ceramic

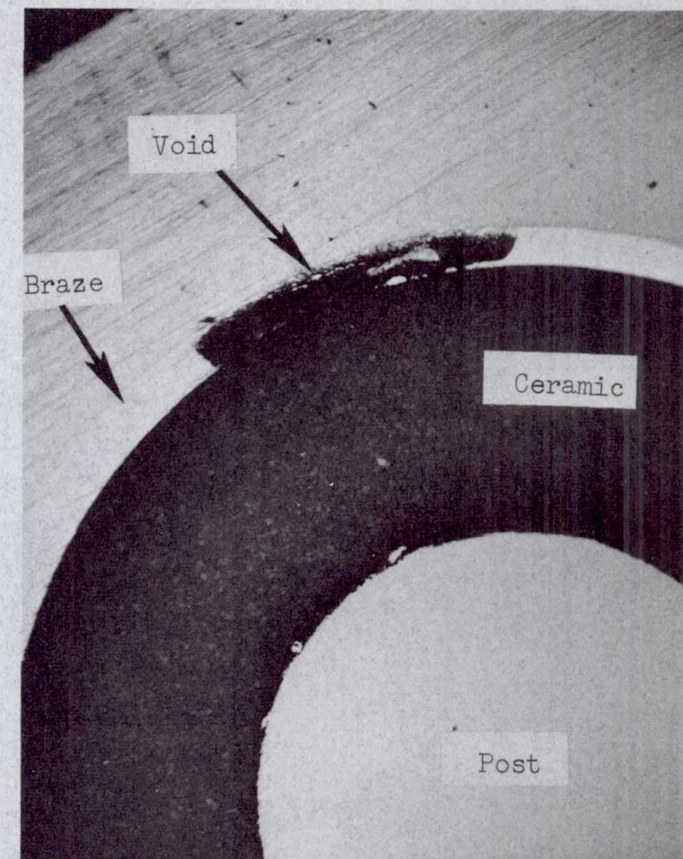

Figure 13. Section of Ceramic-to-Metal Seal Showing Void in Braze

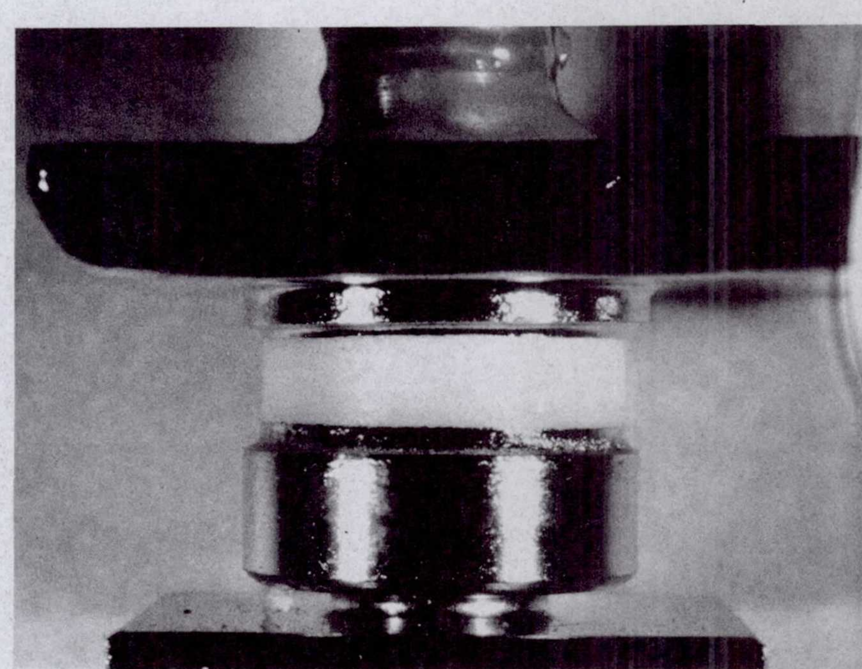

Figure 14. Underside of Terminal Seal
Before Corrosion Test

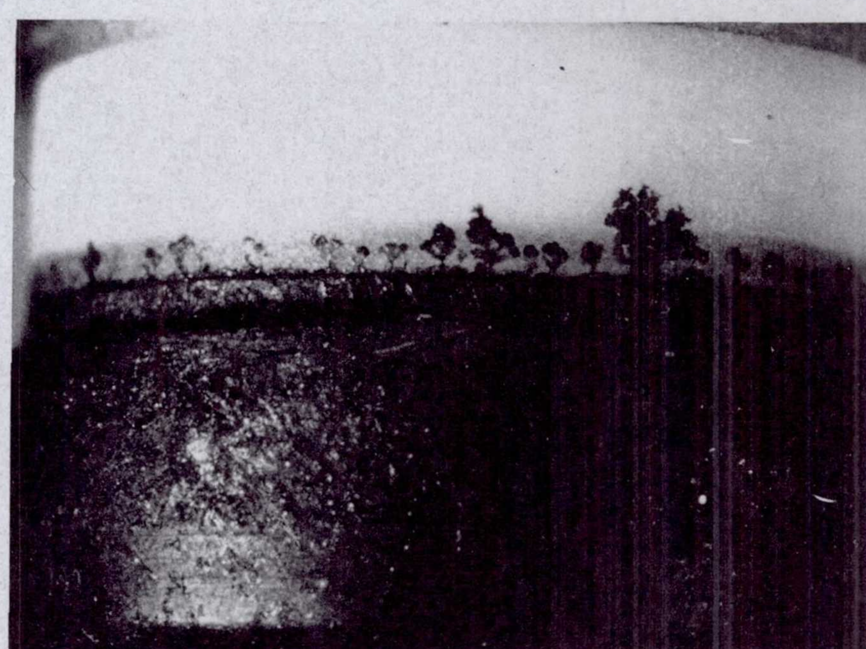

Figure 15. Terminal Seal of Figure 14 After
3 Months on Corrosion Test

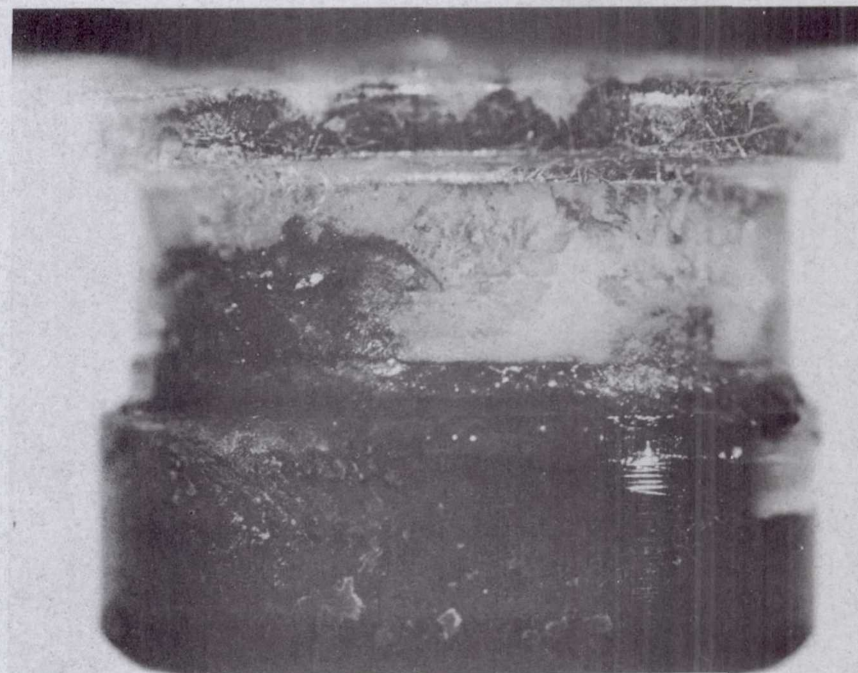

Figure 16. Terminal Seal of Figure 14 After 6 Months on Corrosion Test

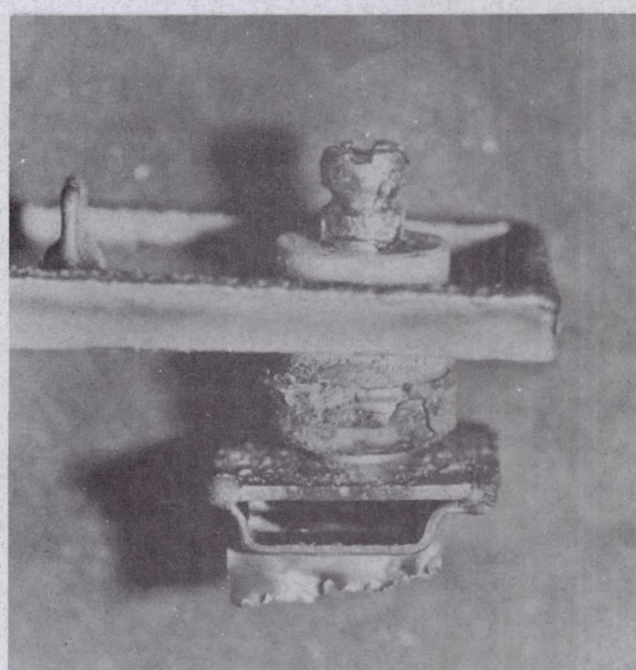

Figure 17. Peeling of Nickel Plating From Terminal Seal During a Cell Test

5. DISCUSSION AND SUMMARY

5.1 ANALYSIS OF GLASS-TO-METAL SEALS

Only seals depending entirely on glass-to-metal joints are discussed here. The triple-seal, containing both glass and ceramic-to-metal seals, is discussed with ceramic-to-metal types.

Test results have shown that uncoated glass-to-metal seals are not suitable for use in alkaline spacecraft cells even for short missions. The glass is subject to cracking, presumably because of stresses induced by the mass of the plates, and the glass-to-metal bonds are relatively rapidly penetrated by the caustic electrolyte. Tests begun several years ago at NAD, Crane showed more than 75% alkaline leakers among failed cells within 1 yr. Users generally concurred with this experience.

The use of coatings to shield the inner surface of the seal from the electrolyte has been tried a number of times without significant success except for short periods of time. Coatings have been found that adhere well to the glass but not to the metal and vice versa, but not to both, presumably due to the creep action of KOH.

In view of the above, additional work on glass-to-metal seals for space-type cells appears unjustified; therefore, comparable low cost with high reliability should be sought in compression seals.

5.2 ANALYSIS OF CERAMIC-TO-METAL SEALS

This section discusses the relative merits of various features of ceramic-to-metal terminal seals intended for use on spacecraft-type nickel-cadmium cells. Design, manufacturing, and test aspects are included.

Alumina is used as the insulation on all terminals now available. Alumina appears to have been chosen for this seal because of its availability and relatively low cost. There is general agreement that the higher the Al_2O_3 content, the better the joints. Silica content is kept as low as possible to minimize reaction with the caustic electrolyte. There is some evidence that even the purest alumina contains some glassy phase (silica), and hence may be vulnerable to KOH over long periods of time.

Other ceramics containing no silica presumably could be used in place of alumina; however, no others have been tried to our knowledge.

A change to a flexible collar between the ceramic and the cell cover by one vendor has resulted in a marked reduction in leak frequency compared to that found in a rigid insulator mounting.

A similar flexible mounting, which has been available on cells from another vendor for several years, has resulted in relatively few leaks caused by stresses. Thus some flexibility in the joint between the cell cover and the terminal insulator is desirable. To provide the necessary flexibility, the stress-relief collars are made of thin material; hence, special attention is required to prevent damage to this part. Corrosion must be prevented or leaks may develop through the metal. The materials used for the collar are chosen primarily to match the expansion characteristics of the insulator, and are less corrosion resistant than the alloys used for the rest of the cell container.

The terminals of this type could benefit from a detailed stress analysis. Points where excessive stress is concentrated in the ceramic-to-metal brazes remain in all current designs, and as such are points where failure is most probable. Most of these areas could be eliminated by refinements in design.

The use of four braze joints in the Gulton and General Electric terminals, any one of which can cause the cell to leak, would appear to be risky. The extra brazes are justified by the vendors on the basis that they allow properly matched alloys to be used for the cup and stress relief member (see Figures 1 and 2), and allow these parts to be made by stamping rather than machining. The result is that tighter dimensional tolerances can be held between the ceramic and the metals and the cost is less. In view of the fact that few if any cases have been reported in which either of the two metal-to-metal brazes (e. g. , E and G in Figure 1) has developed a leak, the approach used is apparently sound.

A configuration in which the terminal post and cup are brazed at the top of the insulator is less likely to develop leaks than one with the cup brazed at the bottom. With the cup at the top the associated ceramic-to-metal braze is separated from the main cell cavity by a narrow path, thus restricting contact with the electrolyte. The enclosure made by the cup (see Figure 2) facilitates use of filler to further limit access of fluid and gas to the inside surface of the upper braze joints. Mounting the terminal post on top of the insulator has one other potential advantage in that, while cells are handled on the earth's surface, the weight of the plates puts the upper brazes and the insulator under compression which is desirable, whereas with the cup on the bottom, the parts are under tension. Once the cells are in space, however, this difference disappears.

The terminal configuration supplied by Gulton presents one additional problem owing to the open void space between the terminal post and the wall of the hole through the insulator. This space tends to trap any liquid contacted by the open end of the crevice, and any trapped material is very difficult to remove. If water is retained for any length of time, corrosion of the inside surface of the lower cup (e. g. , item I, Figure 1) may occur. Several cases of such corrosion leading to leakage of cells has been observed recently, and may be due to entrapment of plating solution during plating of the cover assembly with nickel. Hence special precautions against contact of the upper end of the current Gulton terminal assembly with water are advisable.

The terminal seals currently used by Gulton and General Electric appear to be resistant to shorting by silver migration, although the braze alloys used are not inert in the cell environment. The protective coatings used have been shown to contribute to the integrity of the braze joints for a limited time. Tests made with uncoated braze joints have resulted in bulky black deposits on the braze surfaces but no shorting. As this form of attack can contaminate the electrodes and may contribute to leakage, protective coatings are desirable.

The protective coatings currently used have limitations which may affect the life of the seal. Both the nickel plating, as used by Gulton, and the epoxy resin, as used by General Electric, tend to lose their bond with the metal substrate in the cell environment. With nickel plating the problem has been traced to the presence of titanium or zirconium in the braze. These refractory metals appear at the outer surface by diffusion from the activation layer at the ceramic interface, and weaken the adherence of the plating. Nickel plating is also porous, and does not form a continuous layer over pits in the braze surface. Reaction of braze material with the environment can occur through such discontinuities, contributing further to lifting the metal film.

The bond between metals and epoxy coatings is also vulnerable to attack by KOH. The bond between the ceramic and epoxy coatings is much more resistant, however, allowing the epoxy to inhibit growth of deposits on the insulator even though KOH may reach the braze joints. In view of this analysis and the results of testing to date, the epoxy coating system is preferred.

Other potentially useful organic coatings have not been investigated, especially certain thermally cured systems such as "Penton" and "Kel-F." Polymers cured at elevated temperatures are known to be more chemically resistant than those cured at room temperature. There is no apparent reason why the cover assemblies cannot be heated to the temperatures required to cure these systems.

Sonotone has taken a unique approach to protecting the ceramic-to-metal seal by using glass-to-metal seals (in the triple-seal) instead of coatings. The vulnerability of glass-to-metal seals to the KOH electrolyte has been discussed. The degree to which the inner glass seal prevents access of KOH to the ceramic-to-metal seal during cell tests is not known, as the seals would have to be sectioned to find out. Judging by the frequency of leakage visible from outside the cell during cycle testing, these seals are as effective as either of those discussed above for at least a 2-yr period.

A more basic approach to solution of the corrosion problem involves the use of braze alloys containing little or no silver. Some compromise with corrosion may be necessary to take advantage of the ductility provided an alloy by an appreciable silver content. The tendency toward shorting of the insulator by silver migration appears to have been greatly reduced by going from 100% silver to 78% silver in the silver-copper eutectic used by several manufacturers today. The range of compositions that are practicable is quite limited, as the alloy must satisfy many requirements other than resistance to corrosion to make a ceramic-to-metal joint.

NIORO alloy (see Table 4) contains no silver and has been tried with results that depend strongly on the configuration. Gulton found that NIORO worked poorly on their design, as it resulted in excessive cracking of the ceramic and poor alloying characteristics with the materials used. RCA, on the other hand, has used NIORO or something similar in the configuration shown in Figure 5 and was able to produce a physically sound device. Testing of the latter has been insufficient to indicate its overall applicability to spacecraft cells. Sonotone is successfully using a gold alloy of undisclosed composition which contains no silver in their triple-seal. Metallizing is done by the moly-manganese process in this device, and is probably used in the RCA design. Thus certain terminal seal designs appear to permit use of harder braze alloys, while others do not.

The new terminal design under test at General Electric (Figure 4) bears watching because it contains no silver and is more easily adaptable to a variety of cell sizes and shapes than is the RCA seal or the triple-seal. The main question to be answered by further testing is whether the relatively nonductile "essentially pure" nickel braze material can maintain the braze-to-ceramic bond and yet not result in sufficient residual stress to crack the braze or the ceramic.

The results of tests to date on the three main types of ceramic-to-metal terminal seals commercially available on nickel-cadmium cells indicate that any one of them is capable of providing a 20-cell battery with a reliability of 0.98 at the end of 2 yr, assuming that the seal is the limiting component. Leakage is the predominant failure mode. In the absence of an understanding of the mechanism of penetration of the seal by the electrolyte, failure rates are not predictable; therefore, the capability for a 5-yr mission has not been established. From the point of view of design, the General Electric terminal appears to have the best potential for long life.

5.3 ANALYSIS OF COMPRESSION SEALS

Most users contacted felt that rubber seals should be suitable for space missions of 1- to 2-yr duration, but not for longer periods. These opinions were based on the general knowledge that most elastomers may be expected to degrade in the space environment due to a combination of loss of volatile constituents to the vacuum and radiation effects. Also, elastomers may lose their resiliency and/or "take a set" when held under compression in one position for an extended period. These possibilities indicate that the ultimate integrity of seals made from elastomers may depend largely on the strength and continuity of the bond to the metal parts. Resistance to penetration of the interface by the electrolyte is a key requirement, implying both an inertness to chemical reaction with KOH and oxygen, and the physical ability to resist the powerful creep action of KOH solution.

As large a bonded area as possible is necessary for this requirement. Most tests of this type of seal have involved cylindrical cells with a single seal of the order of 1 in. in diameter. Use in prismatic cells, most of which have an outside thickness less than 0.9 in., will require a significant reduction in seal area, and may cause problems.

Tests to date indicate that a properly designed and fabricated compressed rubber seal (e.g., the Plitt seal) may be expected to provide sufficient reliability for at least 1 yr. The low cost and ease of fabrication of these seals compared to the metal-to-ceramic seals justifies continued development and testing in the attempt to lengthen their useful life in the space environment. Work should be concentrated in improving the resistance of the metal-to-rubber bond to the action of KOH, and on finding elastomers that retain their flexibility in a hard vacuum.

The only form of nonelastomeric compression seal found with promise for use in space missions was the Ziegler seal. Five years life without leakage has been demonstrated by test at Bell Telephone Laboratories. No technical reason is known for not using this seal in spacecraft cells to date. The main question is one of manufacturing feasibility and cost, in view of the critical nature of the threads. A number of samples should be fabricated and tested to clarify this point. It may be that a different thread design, more easily machined, would prove as effective as that in the original design.

5.4 ANALYSIS OF TESTING METHODS

Testing methods currently available for use by manufacturers of spacecraft cells to evaluate hermetic seals are not adequate to meet existing demands. They are capable of determining the integrity of seals during the test interval and immediately thereafter, but are incapable of indicating longer-term performance potential. Leak testing and insulator resistance testing, for example, are used by all manufacturers for quality control on new cells. These tests indicate the quality at the moment, but neither these nor any other type of spot tests known are able to indicate the ability of the seal to maintain the original level of quality in service.

The so-called corrosion tests conducted by vendors in the course of development and qualification of improved seals also cannot be used to predict long-term performance, although the results tend to be interpreted in this way. Also, various accelerated corrosion tests have been used, but the choice of conditions has been arbitrary and the results have been erratic. Therefore, these tests are considered to be of questionable significance and should only be used to compare the behavior of different seal models. Correlation of results with behavior in actual service has not been established.

Thus, it appears that the only test method now available that is capable of giving a valid indication of long-term performance of seals is the life-cycle type test on complete cells. Such tests are time-consuming and costly, and hence, if seal development is to keep pace with the demands for higher reliability and/or longer life, meaningful accelerated test methods must be developed and used. These, as with any accelerated test method, must be based on identified failure mechanisms and rate-controlling processes, neither of which are sufficiently understood at this time for hermetic seals. If, therefore, appropriate accelerated tests are to be implemented, further investigation of failure mechanisms will be required.

Leak testing is the only nondestructive method available to users for checking the condition of seals when working with complete cells. Unfortunately, helium leak testing, which is the only method found that is capable of a quantitative measure of gas leak rate, is not reliable on older cells due to variable loss of helium.

Alkaline leakage testing has been conducted only on a go-no-go basis to date; however, knowledge of the rate of loss of KOH is no less useful than the gas leak rate in judging the significance of a leak. Quantitative measurement of loss of electrolyte under cell test conditions appears to be impractical, however.

A loss of weight is a measure of total loss of material from a cell. This measurement has not been used extensively, largely because of inconvenience and the uncertainty introduced by application of solder to the terminals during testing. Weight losses observed are usually a few grams or less over a year's time; hence, this measurement is useful mainly for long-term tests.

6. CONCLUSIONS

The following paragraphs present the summary and conclusions of this study of the state-of-the-art of hermetic seals.

Of the four types of hermetic seals that may be considered for use on alkaline secondary spacecraft cells (i.e., glass-to-metal, ceramic-to-metal, compression, and rigid plastic-to-metal), ceramic-to-metal seals generally have shown the best results to date and appear to have the greatest potential for high reliability and long life, although certain compression seals are promising and merit further evaluation. Glass-to-metal and rigid plastic-to-metal seals are suitable only for short, noncritical missions.

Most space-quality, nickel-cadmium cells now commercially available are supplied with ceramic-to-metal terminal seals. Three of the four major cell vendors offer only one type and one design of seal with their standard line of cells. This practice complicates the procurement of completely satisfactory cells, as each brand has a different design of seal and different electrical characteristics.

Any one of the ceramic-to-metal seals of the latest design now available from Eagle-Picher, General Electric, Gulton Industries, or Sonotone is capable of providing acceptably high battery reliability for at least 2 yr, provided stringent quality control, inspection, and screening measures are applied. Gulton and Sonotone seals, in their present form, have been available for testing for less than 2 yr, and the data are as yet insufficient to predict ultimate useful life. The Eagle-Picher and General Electric seals, which have been essentially the same for 4 yr, have demonstrated a capability for a 3- to 4-yr life. Further improvements will be required in all seals for sufficient reliability for five or more years service without some form of redundancy of protective circuitry external to the cell.

The primary failure modes shown by ceramic-to-metal terminal seal assemblies are leaking and internal shorting across the insulator. Leakage immediately after fabrication results from incomplete brazing or voids in the braze material; while leakage later in cell life takes place through cracks that occur in the insulator or braze material, or through pores in the bronze-to-ceramic interface. Internal shorts are formed by silver deposits from silver-containing braze alloys. The details of the processes by which the braze-to-ceramic interface is penetrated or silver is deposited on the insulator in a conductive state are not sufficiently understood at this time to allow other than empirical solutions to the problems involved. This situation has resulted in part from inadequate failure analyses.

Leakage of electrolyte through the braze-insulator interface is the most prevalent failure mode of ceramic-to-metal seals at this time. Internal shorting of the insulator has not been observed in cells made within the past 18 months. Insufficient data are available to establish quantitative seal failure rates as separate from cell failure rates. Failure experience with any one brand of seal has varied widely, mostly because of differences in cell specifications, seal specifications, quality control requirements, inspection methods, and acceptance tests employed by cell users. Tight requirements early in life have resulted in low failure rates during testing, indicating that test results to date reflect differences in quality assurance methods more than inherent capabilities of the seals.

Better data are needed before firm conclusions about the capabilities of existing seals can be made. Some of these data can be obtained by minor modifications of current cell life-testing programs. Available data indicate that cell failure during ground testing of nickel-cadmium cells having ceramic-to-metal seals of recent design has been caused more frequently by degradation of electrodes and/or separators than by seal failure. Hence, the work on improving electrode and separator life should be given higher priority than that on improving ceramic-to-metal seals at this time. This conclusion also applies to sealed silver-cadmium and silver-zinc cells.

Leakage or shorting of the terminal seal may or may not lead to failure of the cell, depending on the severity of the seal failure. There is no simple relationship between cell failure rate and seal failure rate. Maximum permissible leak rates for electrolyte and gas and minimum permissible insulator resistance are a function of cell size, mission length, and battery reliability requirement. The amount of electrolyte, oxygen, and/or hydrogen that can be lost from a cell without significantly degrading electrical characteristics and/or life expectancy is not known; hence, currently specified leak rates are based largely on engineering judgment.

The limitations of state-of-the-art terminal seals are due partly to deficiencies in design and partly to inadequate quality control and/or inspection. Current practice is dictated too much by cost and too little by effectiveness to be appropriate for spacecraft applications. Insufficient detailed analysis has been carried out by vendors to identify potential problem areas.

Quality control and inspection test methods practiced by vendors are generally similar, but because they differ widely in detail, direct comparison of results is difficult. Also, the level of inspection varies according to the customer. This situation results largely from the lack of a uniform set of requirements and test standards for the seals.

Quality control and inspection are also hindered by a lack of definitive test methods. Leak testing, strength testing, resistance testing, and visual inspection, as presently performed, are not adequate to assure the level of quality required.

Because sufficient knowledge of the factors governing seal failure rates is lacking, the use of complete sealed cells as test specimens is the only known reliable approach to life testing hermetic seals. Only real-time (full-term) life testing of cells, which is slow and costly, is now conducted; therefore, a reliable accelerated test method is needed that can condense the time scale by a factor of 5 to 10 if demonstrated seal capability is to keep pace with increasing requirements.

The use of a high-silver-content alloy as the braze material in the ceramic-to-metal seal (currently practiced by the two leading suppliers of nickel-cadmium cells) still presents potential corrosion and contamination problems for long-term missions, in spite of the use of protective coatings. Although several configurations of seals without silver in the braze have been fabricated and have passed short-term testing to date, it is not known whether completely successful seals of this type can be made.

The use of two insulated terminals is preferred over one insulated terminal on prismatic cells, and soldered terminals are preferred for all but the largest sizes of cells. The presence of solder lugs on the terminals greatly facilitates wiring of battery packs. Without such solder lugs, reliable soldering directly to the larger terminals of larger cells is difficult. Threaded terminals are considered less reliable because of the need to limit torquing and the possibility of vibration loosening a connection.

Two seals that have not been used in spacecraft cells but show good potential for long-life applications are: (1) the Ziegler compression type seal and (2) a new, vendor-developed ceramic-to-metal seal employing a nonsilver braze alloy and a new metallizing process. The Ziegler seal, which is not commercially available to date, has been made only at Bell Telephone Laboratories for ground tests on sealed alkaline cells. The new ceramic-to-metal seal should be available as an option on spacecraft nickel-cadmium cells provided results of tests now in progress are favorable.

7. RECOMMENDATIONS

The following paragraphs present recommendations derived from the study of the state-of-the-art of hermetic seals.

Nickel-cadmium spacecraft batteries with requirements for high individual cell reliability or life in excess of 2 yr should be built only with cells having ceramic-to-metal terminal seals. These seals must be the latest design commercially available and fabricated under rigorous standards of quality control.

Efforts to improve these seals to meet present and future requirements should comprise the following tasks, with priority in the order listed:

a. Quality control during manufacturing of existing terminal seal assemblies should be considerably upgraded.

b. State-of-the-art seals should be modified to eliminate existing deficiencies in design.

c. The state-of-the-art of ceramic-to-metal bonding resistant to strongly alkaline environments should be advanced by research on the nature of the material formed at the ceramic-to-bronze interface.

Recommendation (a) should be pursued immediately by: (1) developing a set of minimum quality control standards and test methods applicable to ceramic-to-metal seals currently available and (2) making these standards and methods required for cell user contractors procuring nickel-cadmium cells for life testing or for flight, and ensuring that the requirements are imposed on cell manufacturers by users. Recommendation (b) should be implemented by conducting a detailed physics-of-failure and stress analysis of existing ceramic-to-metal type terminal seal assemblies. Recommendations for modifications resulting from such an analysis should be carried out on test samples, and the modified units subjected to comparative tests.

More definitive, nondestructive test methods should be developed to assist in quality control and inspection of seal assemblies. X-ray photographic techniques should be investigated first for their ability to detect voids or other imperfections in the seal.

Life testing of terminal seals should be carried out only with the seals built into complete cells, rather than with isolated seals, until such time as the failure-rate determining processes have been determined. Cells or batteries subjected to life testing should be arranged to permit visual observation for signs of electrolyte leakage, and permanent records of leakage observations should be kept. Visual detection of leakage should be confirmed by means of a chemical alkaline indicator whenever possible.

Methods of accelerated testing of terminal seals should be investigated as part of, or in conjunction with, the study of accelerated cell testing currently under contract to NASA.

Two proprietary ceramic-to-metal terminal seal designs containing no silver or copper and incorporating the "shear-seal" concept should be evaluated. They should be subjected first to accelerated qualification testing, then to life testing as part of whole cells.

Methods and materials used for making ceramic-to-metal seals for applications other than battery cells should be examined in detail for applicability to the alkaline cell environment.

Methods and concepts for sealing large-capacity cells (100 A-hr and over) should be explored in conjunction with new methods of removing heat and minimizing electrical power losses.

Efforts to improve bonded elastomeric type seals should be pursued by performing a study of the mechanism by which KOH solutions attack the rubber-to-metal bond.

The feasibility of use of the Ziegler compression seal in spacecraft cells should be investigated. Ease of manufacture, relative cost, and adaptability to all sizes of cells should be determined in the course of preparing samples for qualification testing.

A universal specification for hermetic terminal seal assemblies for alkaline spacecraft cells should be prepared. This specification should establish minimum requirements for physical strength, rigidity, stress relief, electrical characteristics, leak rate, etc., as a function of cell capacity and life requirement. Suitable test methods should be included where available. Then, appropriate portions of this specification should be incorporated by NASA contractors in procurement specifications for sealed cells and batteries.

8. NEW TECHNOLOGY

No new technology was developed under this contract.

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APPENDIX I

TABULATION OF DATA FROM USER QUESTIONNAIRES

A tabulation of responses to a questionnaire sent to manufacturers and users of sealed spacecraft cells is presented in Appendix I. An independent analysis made by the Materials and Processes Department of TRW Systems served as the basis for specific questions put to vendors. Some of the topics covered by the questionnaire are cell types used, cell configuration, failure mode, mission life, and inspection methods.

TABULATION OF DATA FROM USER QUESTIONNAIRES

1. Cell Types Used

	Ni-Cd	Ag-Cd	Ag-Zn
NRL[1]	1 (See note)		2
RCA[2]	1		2
NAD[3]	1	2	3
Lockheed[4]	1	3	2
JPL[5]	2	3	1
Hughes[6]	1	3	2
Boeing[7]	2	3	1
G.E.[8]	1	3	2
TRW	1	2	3

[1] U.S. Naval Research Laboratories—Washington, D.C. See Appendix II for names of individuals.

[2] Princeton, N. J.

[3] U.S. Naval Ammunition Depot—Crane, Ind.

[4] Sunnyvale, Calif.

[5] Jet Propulsion Laboratory—Pasadena, Calif.

[6] Los Angeles, Calif.

[7] Seattle, Wash.

[8] General Electric—Valley Forge, Pa.

Note: Numerals indicate relative order of importance or frequency.

TABULATION OF DATA FROM USER QUESTIONNAIRES (Continued)

2. Cell Configuration

	Cylindrical	Prismatic
NRL	1	2
RCA	2	1
NAD	2	1
Lockheed	2	1
JPL	2	1
Hughes	2	1
Boeing	2	1
G. E.	2	1
TRW	2	1

3. Type of Metal-to-Nonmetal Seal

	Glass	Ceramic	Rigid Plastic	Other
NRL	2	1		
RCA	2	1		Bonded rubber-to-metal seal (3)
NAD	2	1		Neoprene, etc. (3)
Lockheed	3	2	1	2
JPL			1	
Hughes		1	2	
Boeing		2		
G. E.		1		
TRW		1	2	

TABULATION OF DATA FROM USER QUESTIONNAIRES (Continued)

4. Failure Mode

	Ag Migration	Leak: Metal-to-Nonmetal	Leak: Crack-Nonmetal	Short	Other
NRL	2	1		3	
RCA	3	1			2 Metal-to-metal braze
NAD	4	2	5	3	1 Separator degradation
Lockheed		1	2		
JPL					Leak; crazing of plastic
Hughes		1		2	
Boeing		1	2		
G.E.		1			
TRW	2	1	3		

TABULATION OF DATA FROM USER QUESTIONNAIRES (Continued)

5. Cell Vendor	Yardney	ESB[1]	E-P[2]	G. E.[3]	Gulton	Sonotone	T. I.[4]	Other
NRL	2			3		1		
RCA	5		4	1	2	3		
NAD	x	x		x	x	x		Gould, C&D Delco, Power Sources
Lockheed		x	x		x	x		
JPL	x	x	x		x	x	x	
Hughes	x	x		x	x	x		
Boeing	x	x	x	x	x	x		
G. E.			x	x	x	x		
TRW	x			x	x			

[1] Electric Storage Battery—Raleigh, N. C.

[2] Eagle-Picher—Joplin, Mo.

[3] General Electric—Gainesville, Fla.

[4] Texas Instruments—Attleboro, Mass.

TABULATION OF DATA FROM USER QUESTIONNAIRES (Continued)

6. Mission Life

	<6 months	6 months to 1 yr	1 to 3 yr	>3 yr
NRL		1	2	
RCA		1	2	3
NAD	4	3	2	1
Lockheed	1	2	3	4
JPL	2	1	3	
Hughes	3		2	1
Boeing		1	2	3
G. E.		2	1	
TRW			2	1

TABULATION OF DATA FROM USER QUESTIONNAIRES (Continued)

7. Inspection Methods

	Visual	Microscope	Dimensional	Leak Alkaline	Leak Helium	X-Ray
NRL				x		
RCA	x			x		
NAD	x		x	Immersion seal test		
Lockheed	x			x	x	
JPL	x			x		
Hughes	x			x		
Boeing	x		x	x		
G.E.	x		x	x		
TRW	x	x	x	x	x	x

	Shock	Vibration	Accleration	Pull	Torsional	Compression
NRL		x				
RCA	x					
NAD						
Lockheed						
JPL		x	x			
Hughes	x	x				
Boeing						
G.E.	x	x				
TRW	x	x				

TABULATION OF DATA FROM USER QUESTIONNAIRES (Continued)

8. Are some of the above tests performed after shock and/or vibration?

NRL	Yes
RCA	Yes
NAD	(Blank)
Lockheed	(Blank)
JPL	(Blank)
Hughes	(Blank)
Boeing	(Blank)
G. E.	Yes

9. Tests performed other than those listed in 7.

NRL	(Blank)
RCA	Alkaline indicator test repeated after the battery is assembled
NAD	(Blank)
Lockheed	None
JPL	(Blank)
Hughes	(Blank)
Boeing	Store and see if leak develops with time (alkaline test?)
G. E.	(Blank)

TABULATION OF DATA FROM USER QUESTIONNAIRES (Continued)

10. Most reliable test for determining the effectiveness of hermetic seal.

NRL	(Blank)
RCA	Alkaline indicator test
NAD	(Blank)
Lockheed	Helium leak test
JPL	(Blank)
Hughes	Alkaline leak test following shock and vibration
Boeing	Store and see if leak develops with time (alkaline test)
G. E.	Alkaline leak test after overcharge

APPENDIX II

ORGANIZATIONS AND INDIVIDUALS CONTRIBUTING TO STUDY

Vendor Organizations	Persons Contacted
1. Sonotone Corporation, Elmsford, New York	L. Belove
2. Texas Instruments, Attleboro, Massachusetts	C. Jost, P. Popat, J. Elder, K. Johnson
3. Gulton Industries, Metuchen, New Jersey	K. Preusse
4. Ceramaseal Inc., New Lebanon Center, New York	R. Turner, A. Bledbenner
5. General Electric Schenectady, New York Gainesville, Florida	R. Bondley G. Rampell

Users and Test Organizations	Persons Contacted
1. Bell Telephone Laboratories, Murry Hill, New Jersey	T. Cassotta
2. U.S. Naval Research Laboratories, Washington, D.C.	J. Yuen Wilhelm
3. The Boeing Co., Seattle, Washington	S. Gross
4. Lockheed MSC, Sunnyvale, California	M. Gandel, R. Kinsey, A Miller
5. Applied Physics Laboratories, John Hopkins University, Johns Spring, Maryland	L. Wilson
6. General Electric Space Center Valley Forge, Pennsylvania	M. Read
7. RCA Space Center, Princeton, New Jersey	I. Schulman, H. Thierfelder K. Duncan, R. DeVaux
8. Quality Evaluation Laboratory U.S. Naval Ammunition Depot Crane, Indiana	H. Schultz, D. Mains
9. Jet Propulsion Laboratory Pasadena, California	P. Goldsmith R. Banes
10. Hughes Aircraft Corporation El Segundo, California	D. Weinberger